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ABBREVIATIONS

%	percent	Fg/g	micrograms per gram
<	less than	Fg/ml	micrograms per milliliter
>	greater than	Fm	micrometer (10^{-6} meter); micron
#	less than or equal to		
$	greater than or equal to	mg	milligram (10^{-3} gram)
.	approximately	ml	milliliter (10^{-3} liter)
ACM	advanced composite materials	mm	millimeter (10^{-3} meter)
		mg/L	milligram per liter
AM	alveolar macrophage	mg/m³	milligram per cubic meter
BMI	bismaleimide	4,4'-MDA	4,4'-methylene dianiline
EC	degrees centigrade	MEK	methyl ethyl ketone
cc	cubic centimeters	MMVF	man-made vitreous fibers
CHO	Chinese hamster ovary	MPa	mega Pascals (mega = 10^6). To convert MPa to psi, multiply by 145.
cm	centimeter (10^{-2} meters)		
CO	carbon monoxide		
D_{ae}	aerodynamic equivalent diameter	MSDS	material safety data sheet
		ng/m³	nanogram per cubic meter (nano = 10^{-9})
DGEBPA	diglycidyl ether of bisphenol A		
		NAVOSH	Navy Occupational Safety and Health
e.g.	for example		
EPA	Environmental Protection Agency	NIOSH	National Institute for Occupational Safety and Health
et. al.	and others	NTP	National Toxicology Program
f/cc	fibers per cubic centimeter	OSHA	Occupational Safety and Health Administration
f/m²	fibers per square meter		
f/m³	fibers per cubic meter	PAH	polycyclic aromatic hydrocarbons
f/ml	fibers per milliliter		
g/cm³	grams per cubic centimeter	PAN	polyacrylonitrile
GPa	giga Pascals (giga = 10^9) To convert GPa to psi, multiply by 145,000	PEEK	polyether ether ketone
		PEL	permissible exposure limit
		PPD-T	poly (p-phenylene diamine terephthalate); poly-p-phenylene terephthalamide
HEPA	high efficiency particulate air		
IARC	International Agency for Research on Cancer	PPE	personal protective equipment
i.e.	that is	ppm	parts per million
IH	industrial hygienist	prepreg	preimpregnated
km	kilometer (10^3 meter)	psi	pounds per square inch
L	liter	REL	recommended exposure limit
LDH	lactic dehydrogenase	SCE	sister chromatid exchange
lpm	liters per minute	SEM	scanning electron microscopy
Fg	micrograms (10^{-6} grams)		

SiC	silicon carbide
STEL	short term exposure limit
TWA	time weighted average
v/v	volume/volume
W/cm²	watts per square centimeter
w/v	weight/volume
w/w	weight/weight

INTRODUCTION

Composite materials result from combining at least two different components to yield a new material whose properties differ from the original constituents. For example, concrete is a composite made of gravel and cement. The term took on a new meaning in the early 1960s when the aerospace industry began producing and testing structural components made of resins reinforced with carbon or boron fibers. With the successful use of these lightweight, high performance materials, new terms were coined: advanced composite materials (ACM) and high performance composites.

Loosely defined, advanced composite materials are high performance man-made materials consisting of a fiber reinforced matrix system. ACM can be tailored for specific applications by combining resin and fiber properties to produce the desired weight, temperature resistance, electrical conductivity or strength characteristics. The choice of resins is diverse - epoxy, polyimide, polyurethane, bismaleimide and metals, to name a few - as are the choices for fiber reinforcement - carbon, boron, aromatic polyamide, ceramic, glass and metal. Similarly, ACM applications are almost limitless, from aircraft components, satellite reentry shields and turbine engines to prosthetic devices, fishing rods and musical instruments.

Along with the increasing usage of composite materials came the concern about possible associated health risks. Occupational health personnel were already familiar with the generation of vapors during chemical manufacturing processes such as those encountered during matrix production. The unknown parameters dealt with handling the raw fibrous materials and repairing composites. The heavy use of ACM in aircraft created another problem - what happens to the resins and the fibers during a fire or explosion? Concern escalated because fibrous materials were involved, and the inevitable possible parallel with asbestos fibers arose.

The scientific community began searching for the answers to these questions. However, the advanced composite industry is only about 30 years old - still in its infancy -so research data is limited. Epidemiological studies are almost nonexistent, and until recently, animal studies were conducted using artificial exposure routes. Thus far, the limited experimental evidence suggests potential problems when machining composites and during mishap scenarios involving ACM.

This document summarizes the most current information on advanced composite materials, including chemical and physical properties of the components, exposure issues, regulatory standards and toxicological data. The intention is to provide information that will assist the industrial hygienist, occupational medicine physician and other Navy medical department professionals in making informed decisions about the health hazards associated with ACM.

No attempt has been made to individually identify and discuss all composite components available. Such a document would be monumental; ACM technology, particularly matrix formulations, is still developing, improving and producing new variations. Consequently, matrices are discussed as broad categories, with specific constituents addressed as necessary to alert the reader to associated hazards. The reinforcing fibers are addressed specifically, since the potential for health risk from this component is still unclear.

PRODUCTION AND USE OF COMPOSITES

Elements like carbon, silicon, aluminum and oxygen are known to form strong, stable bonds between atoms. Resultant combinations - aluminum oxide, graphite, silicon carbide - produce materials that are strong, stiff, heat and chemical resistant, yet low in weight. Unfortunately, they are usually too brittle to use in structural applications because a small scratch or internal flaw in a sheet of the material can be enough to crack or destroy its integrity. The solution is to produce the material as individual fibers. This retains the desirable features but drastically reduces the chance that a flaw in a single strand, or even several strands, will compromise the integrity of the product.

Similarly, many resin systems are inherently weak and subject to breakage because of the rigid crystalline bonding patterns. Other resins are too flexible for structural applications due to loosely formed or tangled bonding. However, should the molecules be chemically oriented in the direction of the applied stress, an otherwise unusable resin becomes valuable.

To make an advanced composite material (ACM), the high strength reinforcing fibers are embedded in the preferentially oriented matrix. The final product has been engineered to retain the attributes of the individual components and overcome the deficiencies.

The manufacture of ACM involves producing the resin system, the reinforcing fibers and fillers or additives, joining the system components in a layup procedure and curing or consolidating the laminate, if needed, to cross-link the matrix.

FIBERS

Reinforcement fibers for composite materials have historically been continuous filament, mass fabricated, high modulus and high strength fibers such as carbon, glass, aromatic polyamides and boron. Though these remain the most widely used, the industry has recently been developing and refining applications for metal fibers (wires), ceramic fibers, and the use of short or chopped fibers called whiskers.

In general, initial fiber production processes involve mixing and heating raw materials to produce a melt. The molten substance is then extruded through nozzles or through a series of rapidly rotating wheels that draw or spin the melt into continuous fibers or filaments. The fibers can be further processed into rovings (10,000-40,000 continuous filaments), chopped strands, tapes, mats, yarns (<10,000 continuous fibers), felts, tows (>40,000 continuous fibers) or woven fabric. Fibers can also be wound on spools for use in composite layups.

Fibers can be treated to improve the physical properties, to enhance compatibility with the matrix material or to improve the ease of handling the bulk fiber. Methods to improve fiber-resin bonding include treatment with oxidizers, acids or ammonia that etch or wet the fiber surface. Irradiation, carbon dioxide treatment, electrolyte baths, carbon coating and plasma treatment can also be used to enhance bonding. A fairly recent treatment - whiskerization - actually grows monocrystalline whiskers on the fiber surface to roughen it and increase the bonding area (Sittig, 1980).

Sizings will improve handling, prevent abrading and permit smoother delivery of the fiber during filament winding processes. To increase fiber tensile strength and oxidation resistance, pyrolytic coatings (e.g., pyrolytic graphite, boron, carbide) may be applied or the fibers can be immersed in liquid bromine (Sittig, 1980; Peters et. al., 1981).

Probably the most commonly used fibers are carbon and graphite. Though these two names are often used interchangeably, carbon is the correct term for fibers pyrolyzed at 1000-1200EC - essentially amorphous carbon - whereas treatment at 2200-2700EC produces the crystalline structure known as graphite (Volk, 1978; Zumwalde and Harmison, 1980).

Rayon was the preferred raw material for carbon fibers prior to 1973. Upon heating at 200-350EC, the rayon forms a thermally stable char and undergoes a 50-60% weight reduction. The unstructured char is carbonized by additional heating at 1000-2000EC, during which the incipient carbon layer structure emerges. An optional third heat cycle at 2700-3000EC graphitizes the fiber. Overall carbon yield for the process is 20-25%.

Polyacrylonitrile (PAN) and pitch have replaced rayon as preferred precursor materials. PAN is processed essentially the same as rayon, although it may undergo an initial stretching at about 100EC, which improves the polymer alignment and results in a higher tensile strength of the final product. The stabilization cycle is at 190-280EC, usually in an oxidizing atmosphere, and tension may be applied to the fibers to prevent shrinkage and further align the polymer ladder. Carbonization is done at about 1000-1400EC. Graphitization requires additional heating above 2500EC. Overall carbon fiber yield is 45-50% (Volk, 1978; Holt and Horne, 1978; Peters et. al., 1981).

Lastly, commercial coal tars or petroleum pitch can be heated to the liquid crystal state, then spun or drawn to produce an intermediate, highly oriented fiber. This fiber is then subjected to an oxidizing heat cycle followed by carbonization heating. This process yields 75-85% carbon (Volk, 1978).

Closely following graphite and carbon in commercial use are the aromatic polyamide or aramid fibers. They are made by chemically producing poly (p-phenylene diamine terephthalate), or PPD-T, polymer, which is then spun into fibers. The aramids are probably best recognized by their trade names - Kevlar® and Nomex®, manufactured by

Dupont and Twaron®, made by Akzo. It has been shown that Kevlar® 49 has the highest strength to density ratio of the available reinforcing fibers (Parker, 1990).

Fibrous glass used for composite reinforcement is generally produced by die drawing. This makes a more uniform diameter product than does the spinning process used to manufacture insulating glass. Fibers destined for composite use are usually coated with polyvinyl acetate chrome chloride, polyvinyl acetate-silane, polyester silane or epoxy-silane sizings (Konzen, 1988).

High temperature reinforcing fibers include a variety of metal, metal-carbon and ceramic specialty fibers that are generally used in conjunction with special high temperature resin formulations. Metal fibers, often referred to as wires, are commonly made of boron, beryllium, tungsten, titanium, molybdenum, tantalum and niobium (Hillig, 1978).

Crystalline ceramic fibers are usually used as either continuous filaments or as whiskers for reinforcement of ceramic or metal matrices. The most common ceramic fibers are silicon carbide, silicon nitride, boron nitride (Bye et. al., 1985) and aluminum oxide polycrystalline whiskers (Hillig, 1978). Ceramic fibers are treated with a bonding enhancer or used with an alloyed metal matrix to promote proper wetting and ensure good fiber-matrix bonding.

Bicompound or hybrid fibers are made by depositing carbon on a finished fiber of another material, or by depositing a second material onto a finished carbon or graphite fiber (Sittig, 1980). Examples include carbon-boron, carbon-tungsten, carbon-glass, graphite-aluminum, carbon or graphite-Kevlar®, graphite-silica and graphite-steel.

RESINS

Though there are many resins or matrices for advanced composite materials, they can be loosely grouped into thermosets, thermoplastics and high temperature resins. Thermosets are designed to be liquids or semisolids that have viscosities low enough to infiltrate the volume between the fibers, thus forming a homogeneous and continuous "glue" for the composite (Kantz, 1989). After heat curing, these resins irreversibly harden into cross-linked solids. The most commonly used resin - epoxy - is a thermoset, as are polyurethanes, polyimides and phenolic resins.

The newer thermoplastics include polysulfones, polystyrenes, polypropylenes and polyesters. These do not form rigid crosslinks, but rather can be heated and reshaped repeatedly. Although this makes them less stable at high temperatures, it offers great advantages for composite repair operations. Thermoplastics offer about the same chemical resistance and low temperature thermal performance as do the thermosets, but offer added damage resistance capacity (Thayer, 1990).

Listed below are some common thermoset and thermoplastic resin systems (compiled from Hillig, 1978; Sittig, 1980; Zumwalde and Harmison, 1980; ASM, 1987; SACMA, 1989):

Thermoset Resins	Thermoplastic Resins
Polyimide (PI) (i.e, bismaleimide)	Polyphenyl sulfide
	Polyester
Phenolic	Polyamide
Polyester	Polysulfone
Epoxy	Polyarylsulfone (PAS)
Polyurethane	Polyether etherketone (PEEK)
Melamine and urea formaldehydes	Polyetherimide
	Polymethyl methacrylate
	Polyethylene
	Polypropylene
	Polystyrene
	Polycarbonate
	Styrene-acrylonitrile

Some resins, such as the polyimides and polyamideimides, are called pseudo-thermoplastics. These systems can be formulated as either thermosets or thermoplastics, depending on the production reaction.

High temperature resins are currently manufactured for special purpose aerospace applications. The basis for these resins is usually a metal, which can provide considerable improvement in the composite's strength and toughness. However, this is offset by the increase in composite weight. Typical matrix metals include aluminum, magnesium and titanium, with aluminum favored for its corrosion and oxidation resistance (Hillig, 1978; Chou et. al., 1986). Metals complexed with carbon, silica and silicon carbide are also being researched and tested for aerospace use.

Following are some commercially available metal and metal hybrid matrix resin systems (compiled from Hillig, 1978; Chamis, 1981; Chou et al., 1986):

Aluminum	Aluminum-carbon	Aluminum-silica
Copper-tungsten	Titanium	Carbon-magnesium
Nickel-carbon	Magnesium-boron	Zinc
Lead	Titanium-aluminum	Copper(chromium)-tungsten
Copper-aluminum	Niobium	Lead
Nickel-tungsten	Aluminum-boron	Aluminum-silicon carbide
Magnesium	Titanium-boron	Tin
Silver-aluminum	Copper	Copper(titanium)-tungsten

Other high temperature resins noted for service in environments up to 1700EC are the ceramics. Though the ceramics are stiff and strong, they are somewhat brittle. Their use is also limited because they cannot be easily melted for infusion into the reinforcing fibers. Rather, they must undergo special high temperature and high pressure sintering processes that consolidate the ceramic powder with the fibers (Chou et. al., 1986). Consequently, ceramic matrices are presently cost prohibitive.

Resin systems often include additives to help control the characteristics or behavior of the material. For example, diluents can be used to change the resin viscosity during pro- cessing or during fiber impregnation. Nonreactive diluents evaporate during the curing process, whereas reactive diluents actually participate in the cure and contribute to the final polymer structure (Kowalska, 1982; Parker, 1990). The thermosets usually have hardeners added - most commonly aromatic or aliphatic amines. Other additives can include accelerators, fillers (e.g., clay, calcium carbonate, diatomaceous earth), dyes, softeners, shrinkage resistors (e.g., beads, particulate minerals), fire retardants, smoke suppressors and release agents (Kantz, 1989).

Some of the commonly used chemical additives are (compiled from Hillig, 1978; McGarry, 1981; Kowalska, 1982; SACMA, 1989):

Nonreactive diluents - acetone, methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, methylene chloride, dimethylformamide, methyl cresol, N-methyl pyrrolidone

Reactive diluents - phenyl glycidyl ether, cresyl glycidyl ether

Accelerators - boron trifluoride mono ethylamine, phenols, alcohols, Mannich bases

Hardeners/curing agents - diaminodiphenyl sulfone (DDS), 4,4'-methylene dianiline (4,4'-MDA), dicyanodiamide (DICY)

LAYUP AND CURING

Once the fiber and resin components of the composite system are ready, they must be joined and processed to form the desired end product. Though procedures vary depending on the fiber, the resin and the ultimate use of the composite, joining is done using either fabrication, preimpregnation or specialized methods.

Fabrication, or wet layup, involves applying resin, either by hand or in an automated proc- ess, to preplied broadgoods. The dry fibers are put in a mold or on a form, then the resin is worked into the fibers.

For thermoplastics, resin transfer or injection molding is often used. This involves putting the fibers into a mold, injecting the resin, then curing the assembly (McGarry, 1981; Thayer, 1990). General Electric developed a variation of this process for producing silicon carbide reinforced silicon. A graphite preform is infiltrated with liquid silicon. The molten silicon reacts with the filamentous graphite to form polycrystalline silicon carbide fibers, with the excess silicon remaining as the matrix. This procedure has been especially successful in making motor shrouds (Katz, 1980).

Preimpregnated (prepreg) tapes or fabrics having uncured resin already embedded in the fibers can be layered in or on the desired mold. However, thermoset prepregs require refrigerated storage to prevent curing, decrease the chance of water absorption and eliminate contamination of the tacky resin.

For layup of some composites, high temperature foils of aluminum, tantalum or copper alloys are interleaved in the laminate to increase transverse strength. These are called ternary composites. The figures below illustrate the dramatic strength differences produced by this process (Hillig, 1978; Chamis, 1981).

Composition, volume	Relative	Strength parallel to fibers, MPa	Strength ratio, transverse to
50% boron fiber, 50% aluminum matrix	100	1138 (165)	0.12
40% boron, 30% titanium-aluminum foil, 30% aluminum matrix	120	1034 (150)	0.43

During fabrication and prepreg layups, the fibers can be preferentially aligned in successive layers of the laminate to produce the desired strength and stress resistance. For example, aligning all the fibers produces a product whose strength in the direction transverse to the fibers is much less than that parallel to the fibers. In addition, when com-posites are made using whiskers, only the concentration - not the orientation - of the reinforcing material is controllable (Hillig, 1979).

The geometry of the reinforcing fibers also affects the properties of the final composite. Most high performance composites use long, continuous fibers (average aspect ratio 100:1), usually bundled into yarn. This ensures resistance to high stress (Chou et. al.,

1986). The fiber orientation can be precisely controlled such that maximum reinforcement is available where maximum stress will occur.

To further increase impact resistance and strengthen the matrix reinforcement, fibers are available as woven, braided or knitted fabrics that can eliminate the planes of weakness inherent when using yarns or tows. The fabrics can be machined into final form, or the fibers can be woven or braided into the desired three dimensional shape.

There are several specialized procedures for making composites. Carbon-carbon components used in the space shuttle thermal protection system are produced in what amounts to a single step. The precursor fabric is impregnated with resin, laid on the mold, then heated to carbonize the fibers. After rough trimming, the part is pyrolyzed at about 900EC to carbonize the resin. The part can then be reimpregnated and reheated up to four times to achieve the flexural strength and heat resistance needed (Chou <u>et. al.</u>, 1986; Colucci, 1990).

Special layup procedures are also needed to make many of the metal matrix composites because of potential reactions between the fibers and the resin. Should there be solubility or chemical changes of either component, the resultant part could be structurally compromised. If the reaction zone is large, the mechanical integrity of the composite can be substantially affected.

Because the high temperatures of metal molten resins can cause the fibers to partially melt, special methods were developed to embed the fibers in the metal powder. This is followed by sintering and hot isostatic pressing to yield the composite. The metal powder-fiber mixture can also be consolidated by subjecting it to high pressure while keeping temperatures below that of the metal's melting point (Sittig, 1980; McGarry, 1981; Chou <u>et. al.</u>, 1986).

Similarly, many ceramic composites must be fabricated using high pressure, since most of them will not melt. As previously discussed, special coatings or wetting techniques may be required to achieve the desired bonding between the reinforcing material and the resin (Chou <u>et. al.</u>, 1986).

Other layup methods include: (1) sprayup - a specialized procedure that uses handheld "guns" to shoot chopped fiber and liquid resin against the mold surface (Hillig, 1979; McGarry, 1981); (2) filament winding - a mandrell or form is rotated about its axis while continuous yarn or roving passes through a liquid resin bath and is then wet wound onto the form. The winding is done in complex patterns to ensure even strength distribution throughout the composite part (McGarry, 1981); (3) pultrusion - continuous fibers are drawn through an orifice where the resin is metered out. The part is formed while maintaining tension on the fibers to enhance alignment (Hillig, 1979); (4) transfer molding - pistons force the composite mixture to flow from a reservoir into a hot mold cavity; (5) centrifugal casting - a variation of filament winding where prewoven braids or sleeves of

reinforcement are impregnated with liquid resin. Centrifugal force is used to ensure even coating; (6) reinforced reaction injection molding - two or more liquid component streams are forced under pressure into an impingement chamber where they are mixed. The resin is then forced into a mold cavity under low pressure. This is often used with polyurethane resins (McGarry, 1981); and (7) thermoforming - a thermoplastic resin technique where the preimpregnated tape or fabric is heated to the softening point, then quickly laid over the forming tool or in the mold where it rehardens to the desired shape (Thayer, 1990).

The newer developmental polyimide pseudothermoplastics can be melted and mixed with the fiber in one step. The viscosity is controlled such that the mix can be pumped immediately into the mold, the catalyst added, and the polymerization process begun (Thayer, 1990).

Regardless of the method used to join the fibers and the resin, thermosets and some specialty resins will require curing. This involves high temperature and/or pressure to crosslink the matrix polymer and consolidate the laminate. Curing conditions vary depending on the resin used. For example, the process can require heating at 65-343EC for as little as one hour or as long as 24 hours (Thayer, 1990). According to McGarry (1981), adding pressure of 3.5 to 13.8 mega Pascals (MPa) (500-2000 pounds per square inch (psi)) at temperatures of 120-175EC can lower the cure time to 15 to 90 seconds.

Before curing, the composite parts or sheets may be enclosed in airtight bags and have separator films (e.g., made of fibrous glass) placed over the laminate. The dry fibers in the separators provide channels for escaping volatiles and help absorb excess resin during the cure cycle. In addition, autoclaves typically have vacuums to draw off the volatiles. Nitrogen gas is usually added to the heating chamber to decrease the chances of an exothermic reaction.

After curing, any coverings or films are removed from the composite. The part can then undergo additional processing cycles in post cure-ovens. When the resin is fully crosslinked, the composite is ready for inspection to detect voids and delaminations, followed by final machining to cut, trim or shape the desired part.

Though the combination of fibers and resins is endless, some of the more common systems are listed below to provide an appreciation for the magnitude of the advanced composite industry.

Matrix	Reinforcing Material
Polymer (i.e., epoxy)	Carbon, graphite, Kevlar®, S glass
Carbon	Graphite
Aluminum-boron or titanium-boron hybrid	Aluminum oxide
Titanium	Boron, silicon carbide coated boron, silicon carbide, beryllium
Iron, cobalt, nickel	Metal wire alloys (molybdenum, tungsten, tantalum, niobium)
Glass	Carbon, silicon carbide
Ceramics	Metal wire (tantalum, tungsten, molybdenum), carbon, silicon carbide
Silicon	Carbon, silicon carbide
Aluminum	Titanium, aluminum, boron, steel, graphite, silicon carbide
Magnesium	Aluminum, graphite, boron
Niobium	Graphite, tungsten
Lead	Aluminum, graphite
Copper	Graphite, tungsten, aluminum
Nickel	Graphite, steel
Tin, Zinc	Graphite

(compiled from Hillig, 1978; Chamis, 1981)

COMPOSITE USE

Advanced composite consumption for 1965 was around two million pounds. In 1989, usage was up to 30.7 million pounds. Estimates for use by 1999 are 68.4 million pounds (Forrest, 1989). Market distribution of composite materials has remained relatively constant, with 75-80% used in the aerospace industry, 10-15% for recreational use, 5-15% in industrial applications and about 5% for the automotive and miscellaneous sectors (Forrest, 1989; Thayer, 1990). However, Forrest (1989) predicts that future usage will balance out more evenly between aerospace and industrial applications due to continued decreases in military budgets.

Thayer (1990) also reports that carbon fiber usage, with 55% of the market, far exceeds that of other reinforcing materials. The remaining distribution allots 25% to aramids, 20% to fibrous glass, and less than 5% to the specialty fibers. Cost is of prime consideration here since carbon fiber production can cost as little as $10 per pound. Contrast this figure with specialty fibers that can be as high as $500 per pound. Since most composites average 60-75% reinforcement material by weight, manufacturing costs remain the driving influence on which fiber is chosen.

Advanced composite usage is as diverse as the available component combinations. It varies from pipes to prosthetics and from parachute tapes and webbings to golf clubs. The following are some of the uses, listed by general category (compiled from DuPont, 1976; DuPont, 1978; Sittig, 1980; McGarry, 1981; NAVMEDCLINIC Norfolk, 1985; Smith, 1986; Kitfield, 1988; AMSO, 1989; Esmen and Erdal, 1990; Thayer, 1990).

Automotive - brake linings, drive shafts, rotary engine seals, tire cords, wheels

Electric - brushings, conductive papers and plastics, voice coils, electrodes, electron shields, heating elements, radar absorbers, superconductor cables, thermocouples, control panel housings, switch gears

Medical - blood filters, medical and dental prosthetics, X-ray appurtenances

Recreational/sports - archery bows, fishing rods, golf club shafts, skis, hockey sticks, musical instruments, racing paddles, tennis rackets, bicycle parts

Mechanical/Structural - Aircraft parts: bearings, brakes, rotors, flywheels, gaskets, turbine engines, radome tails, flaps, rudders, stabilizers, fairings, wings, fuselage. Some aircraft using composites are: C-17 transport, A-12 attack plane, V-22 Osprey tilt rotor, AV-8B Harrier, LHX helicopter, commercial MD11, 767X and 757 jets, F-14 Tomcat, F-15 Eagle, F-16 Falcon, FA-18 Hornet, A-6E Intruder, H46 and H53 helicopters, F111, B-1B bomber and P3 .

Satellites - reentry shields, Hubble telescope support structures
Rockets - fuel tanks, motors and casings
Ships - hulls, secondary structures, decks, superstructure components
Cars - gear selector forks and chassis for Formula One race cars
Miscellaneous - tanks, textile machinery, ropes and cables, conveyor belts and hoses

Miscellaneous - asbestos replacement material, helmets (Kevlar®), pipes, ducts, fittings, explosive storage facilities, protective apparel (e.g., gloves, ballistic protection)

CHEMICAL AND PHYSICAL PROPERTIES

   The properties of the finished composite are a function of the original fiber material, the fiber arrangement, the percentage of fiber used, the matrix material and such manufacturing variables as heating temperature and pressure and the curing environment. However, it is possible to evaluate the chemical and physical properties of both the individual components and the completed composite material. The common fibers will be discussed first, followed by the resin groups. Lastly, we'll compare features of composites as a whole.

FIBERS

   Since fiber size is the major issue from a health standpoint, it is important to note that composite reinforcement fibers, like the man-made vitreous fibers, generally break transversely when abraded. This means that the fibers are still larger than what is generally considered respirable. However, a few studies have shown that carbon/graphite and Kevlar® aramid fibers do undergo some longitudinal splitting or peeling when abraded. Such evidence will be discussed below.

Carbon and Graphite

   Longitudinal splitting of carbon fibers has been reported during sanding, sawing and milling operations (Wagman et. al., 1979; Esmen and Erdal, 1990). The resultant fibers are 3-7Fm in diameter. Further evidence of this phenomenon was provided by Siebert's (1987) ball milling studies.

   Ball milling was used to simulate machining operations. Samples of woven carbon cloth were cut with scissors to 1 cm lengths, then weighed, milled, water extracted, filtered and dried. The resultant material was sized by light microscopy, with only those particles having $3:1 aspect ratio counted.

   The initial fibers had a mean diameter of 7.1Fm. The milled samples were mostly nonfibrous, although 82% of the dust had diameters #3Fm after 30 minutes of milling. The experimental data is summarized below. Fibrous glass samples, known to split transversely only, were evaluated as a reference. The data represents the average of three milling samples for each time period.

Total time ball milling, minutes	% Carbon dust with diameter <3Fm	% Glass dust with diameter <3Fm
5	72.6	76
15	75.7	68.2
30	82.1	69.2

These results show carbon's shift to smaller fiber diameter as milling time increases. For carbon, 46% of the fibers were 0.5Fm diameter by 1.5Fm long after 30 minutes of milling; 39% of the fibrous glass samples were this size after 30 minutes. (Note: The authors attribute the inconsistency in the 5 minute glass results to the large variance between the three sets of data. Standard deviations varied from 0.7 to 21.1 for these results).

A similar ball milling study by Assuncao and Corn (1975) examined fibrous glass and chrysotile asbestos particle size distributions for those fibers having $3:1 aspect ratio. They found that there was essentially no decrease in glass diameters (50% ±3.3% of fibers <2.94Fm diameter initially versus 50% ± 3.5% of fibers <2.80Fm diameter after 12 hours), whereas the chrysotile showed a significant diameter decrease - from 80.9% ± 4.3% having <0.96Fm diameter initially to 90.2% ± 4.5% with <0.96Fm diameter after 12 hours milling.

Combining this information with his findings, Siebert (1987) concluded that both carbon and glass initially fracture transversely, but carbon fragments then undergo some longitudinal cleavage. The fibers produced from this fracture behavior have aspect ratios <10:1. In comparison, chrysotile exhibits progressive longitudinal splitting, producing fibers with aspect ratios that are all >10:1.

As previously discussed, carbon fibers are made by pyrolysis of precursor strands. Subjecting the carbon fibers to higher temperatures (2200-2700EC) results in the more organized crystalline structure that is called graphite. As shown below, the fiber's ultimate characteristics are influenced by the precursor material that is used (Volk, 1978; Hillig, 1979; Chamis, 1981; McGarry, 1981; Diefendorf, 1987; Thayer, 1990).
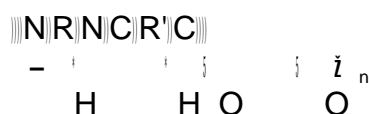
	Rayon	PAN	Pitch
Density, g/cm³	1.43-2.0	1.7-2.0	1.99-2.15
Tensile strength, MPa (x 10^4 psi)	345-690 (5-10) High modulus - 260 (3.8) Very high modulus - 350 (5)	2210-2340 (32-34)	1380-3100 (20-45)
Tensile modulus, GPa (x 10^6 psi)	21-55 (3-8) High modulus - 517 (75) Very high modulus - 689 (100)	170-280 (25-41) 350-520 (51-75) if heated at 2500EC	340-690+ (49-100)
Melting point, EC	3650	3650	3650
Typical diameter, Fm	7	7	7
Additional comments: PAN fibers are 92-95% carbon by weight. Any fibers having a modulus >345 GPa (50 x 10^6 psi) are $99.5% carbon by weight.			

Carbon and graphite are low density, high tensile strength, high stiffness fibers with good corrosion resistance and a low coefficient of thermal expansion. Graphite is theoretically five times more rigid than steel, though in practicality the figure is closer to two times the rigidity (McGarry, 1981).

The average carbon fiber diameter is 6-9Fm (Kowalska, 1982; Esmen and Erdal, 1990). The smallest diameter reported is 4Fm (Winters, 1984; Diefendorf, 1985) and fibers with diameters as large as 25Fm have been produced (Hillig, 1979). Because the fibers are so small, they are usually used as tows having up to 60,000 monofilaments. Yarns, having 1000-3000 filaments, are also commonplace (Hillig, 1979; Chamis, 1981).

Aromatic polyamides

Aramids are long chain polymers that are partially alkaline (the amide) and partly acidic (carboxyl group). The chemical and physical properties vary, dependent mainly on the position of the amide groups. Para structures (i.e., Twaron® by Akzo and Kevlar® from DuPont) are almost 100% crystalline. Nomex® (DuPont) is a meta-aramid. Other aramid trade names include: X500 (Monsanto), HM50 (Teijin-Conex), and Vanilon (produced in the Soviet Union).

The aramid chemical structure is:

Poly-p-phenylene-terephthalamide (PPD-T)

$$-\left[\overset{|}{\underset{H}{N}} \; R \; \overset{|}{\underset{H}{N}} \; \overset{|}{\underset{O}{C}} \; R' \; \overset{|}{\underset{O}{C}} \right]_n$$

where: $R = (CH_2)_6$ $R' = (CH_2)_4$

Longitudinal "peeling" - the production of fibrils that peel away from the fiber surface - has been reported by Lee et. al. (1983) and Reinhardt (1980) during abrasion of Kevlar® pulp fibers. This results in ribbon-like branched and curled fibrils that may stay attached to the parent fiber, or can break off during subsequent machining or handling. As manufactured, aramids have nominal diameters of 12Fm. The fibrils are reportedly <1-3Fm in diameter (Vu, 1988). No such occurrence has been reported for any other aramid fiber.

Aromatic polyamide fibers have a highly oriented crystalline substructure that makes them very strong longitudinally. However, the relatively weak bonds between the crystal domains lead to the microfibril ropelike structure in the individual filaments.

Aramids have the highest overall strength to density ratio of the composite reinforcing fibers. In fact, Parker (1990) states that aramids are five times stronger than steel. Unfortunately, their transverse strength and their stiffness to density ratio are relatively low. The stiffness is less than that of carbon and between that of glass and steel. Though much lighter than glass, aramids will absorb more energy before breaking.

The following aramid information was taken from DuPont (1976), DuPont (1978), Hillig (1979), McGarry (1981), Pigliacampi (1987) and Lee et. al. (1988).

Fiber	Density, g/cm³	Tensile strength, MPa (x 10^4 psi)	Tensile modulus, GPa (x 10^6 psi)

Aramids (as a group)	1.44	2800 (41)	103-152 (15-22)
Kevlar® 49	1.44	2860-4100 (41-59)	124-135 (18-20)
Kevlar® 149	1.47	3400 (49)	186 (27)
Kevlar® 29	1.44	3750 (54)	64-83 (9-12)
HM50 (Teijin, Ltd.)	1.39	3100 (45)	81 (12)

Because aramids begin to decompose at about 500EC, they cannot be used for high temperature applications. In general, the aramids are known for excellent resistance to solvent attack and to corrosion. The fibers will not melt, nor will they sustain combustion in a normal atmosphere if the combustion source is removed (DuPont, 1976; DuPont, 1978; Reinhardt, 1980).

The strong electrostatic properties of dry aramid fibers, together with their hygroscopic nature, means that fiber manufacturing and storage conditions must be carefully controlled. The storage atmosphere is generally maintained at 10-35EC and 25-80% relative humidity (DuPont, 1986; Parker, 1990).

Fibrous Glass

Fibrous glass provides a strong and environmentally resistant reinforcing material. Its high strength and low cost advantages also help outweigh the fact that it is extremely dense in comparison to the other commonly used fibers.

Most reinforcement glass is made from E glass, which has a low alkaline content and serves as a good electrical insulator. If more stiffness is needed, S glass provides a 20% improvement over E glass, but is more costly to process.

The major constituents of the different glasses are summarized below (from Watson and Raghupathi, 1987):

Glass*	Component Material, Weight %							
	Silica	Al	Ca ox-ide	Mg	Boron oxide	Ca_2CO_3	$CaFl_2$	Minor oxides
E	54	14	20.5	0.5	8	1	1	1
A	72	1	8	4	-	14	-	1
S	61	11	22	3	-	0.6	-	2.4
ECR	64	25	-	10	-	0.3	-	0.7

* E glass = electrical grade. Excellent electrical properties and durability.
 A glass = high alkali content. Especially good for reinforcement. Good chemical
          resistance.
 S glass = high strength. Noted for high tensile strength and high thermal stability.
 ECR glass = E glass modified for high chemical resistivity. Good electrical properties.

The properties of the glass reinforcing fibers are summarized in the following table (from Hillig, 1979; Watson and Raghupathi, 1987; IARC, 1988; Bennett, 1989):

Glass	Density, g/cm^3	Tensile strength, MPa (x 10^4 psi)	Modulus, GPa (x 10^6 psi)
S	2.49	4586 (66.5)	83-86 (12-12.5)
E	2.58	3450 (50)	72.5 (10.5)
A	2.50	3040 (44)	69 (10)
ECR	2.62	3625 (53)	72.5 (10.5)

Note: Thayer (1990) reports that there is a new high performance glass being tested that has a tensile strength beyond that of S glass.

Typical diameters for reinforcing glass are 9-24Fm, although fibrous glass as a group (i.e., including insulation glass materials) can range from 0.8 to 25.5Fm in diameter.

Assuncao and Corn (1975) conducted a milling experiment to determine whether fibrous glass was subject to longitudinal splitting. The parent fibers, sized as having an aspect ratio of >3:1, were milled for up to 12 hours. Samples were taken for sizing at timed intervals. Results showed no significant differences in glass diameters throughout the milling, but did show a progressive decrease in fiber length as milling time increased.

The authors also found that the fiber to particle ratio after 12 hours of milling was 4.5% (numbers of fibers and particles not given), whereas the beginning sample was essentially 100% fibrous. The chrysotile asbestos control sample remained fibrous throughout the milling process.

Metal Fibers

Metal reinforcement fibers or wires are extremely coarse, having typical diameters about 25-145Fm (Hillig, 1978). They are particularly useful when high temperature resistance is needed. Though the tensile strengths and modulus data in the chart below (adapted from Chamis, 1981; Bascom, 1987a; Schoenberg, 1987) look impressive when compared with the fibers discussed previously, keep in mind that on an equal weight basis, the metals are only slightly stronger than carbon.

Metal	Density, g/cm³	Tensile Strength, MPa (x 10⁴ psi)	Tensile Modulus, GPa (x 10⁶ psi)	Typical diameter, Fm	Melting point, EC
Boron	2.57	3600 (52)	400 (60)	100	2300
Boron	2.49	3600 (52)	400 (60)	140	2300
Aluminum	2.71	290 (42)	68.9 (10)	--	659
Beryllium	1.85	970-1300 (14-19)	221-310 (32-45)	75-125	1278
Tungsten	19.3	2890-4000 (42-58)	345-407 (50-59)	25-300	3410
Copper	8.9	2890 (42)	345 (50)	--	1083
Molybdenum	10.2	2200 (32)	331 (48)	25	2622
Tantalum	16.88	1520 (22)	190 (28)	500	3000
Steel	7.2	4100 (60)	200 (29)	75	1400
Aluminum whiskers	4.0	1000-2000 (14.5-29)	700-1500 (102-217)	--	--

Ceramics

Ceramic fibers are grouped as oxides, carbides or nitrides. The fibers are commercially available as continuous filaments and as discontinuous fibers or whiskers. Though the continuous fibers provide the highest degree of reinforcement, whiskers have been particularly effective for reinforcing metal and ceramic matrices (Johnson and Sowman, 1987).

In the ceramic characteristic table (page 21), notice the diameters. This is the only group of reinforcing materials that contains commercially produced fibers of respirable size.

Specialty Fibers

The possible combinations of the previously discussed fibers are endless. Some of the more notable examples are shown below (Hillig, 1979; Chamis, 1981).

Characteristic	Specialty Fiber			
	Boron/tungsten core	SiC/carbon core	Boron on carbon	SiC on tungsten
Density, g/cm³	2.49-2.63	3.2	2.21	3.32
Tensile strength, MPa (x 10^4 psi)	2800-3600 (41-52)	2800-3450 (41-50)	3450 (50)	3100 (45)
Tensile modulus, GPa (x 10^6 psi)	400 (58)	400-482 (58-70)	360 (52)	430 (62)
Diameter, Fm	100-200	100	100-200	100-200
Melting point, EC	2100	2690	2100	2690

CERAMIC FIBER CHARACTERISTICS

Representative fiber[*]	Density, g/cm³	Tensile strength, MPa (x 10⁴ psi)	Tensile modulus, GPa (x 10⁶ psi)	Diameter, Fm	Use temp., EC	Melting temp., EC
Oxides:						
95% Al_2O_3/5% SiO_2 - D	3.3-3.5	1000-2000 (14.5-29)	297 (43)	3.0	1600	>2000
52% Al_2O_3/48% SiO_2 - D	2.73	1900 (27.6)	100 (14.6)	2-3	1260	1790
40% Al_2O_3/50% SiO_2/5% CaO/ 3.5% MgO/1.5% TiO_2 - D	2.54	--	--	3.5	875	>1648
92% ZrO_2/8% Y_2O_3 - D	5.6-5.9	--	--	4-6	2200	2600
62% Al_2O_3/14% B_2O_3/24% SiO_2 - C and D	2.75	1720 (25)	155 (22)	3.5-11	1200	1800
42.5% Al_2O_3/2.5% Cr_2O_3/55% SiO_2 - D	--	--	--	3.5	1425	>1760
70% Al_2O_3/2% B_2O_3/28% SiO_2 - C	3.1	2240 (32.5)	207-241 (30-35)	11	1430	>1800
97.9% SiO_2/2.1% miscellaneous oxides - NA	2.1	210-410 (3-6)	72 (10.5)	--	1095	>1760
Carbides:						
SiC (about 54% Si/12% O/ 30% C/3.9% other) - C	2.55	2500-3900 (36-57)	180-400 (26-58)	10-15	1200	>1425
SiC (. 100% SiC) - W	3.2	200-1400 (3-20)	>500 (72.5)	.05-10	--	>1425
Nitrides:						
Si_3N_4 - W	3.2	1500 (22)	350-390 (51-57)	.2-1.6	--	--
Boron nitride - NA	1.8-2.0	300-1400 (4.4-20)	28-80	--	--	--

[*]D = discontinuous fibers   C = continuous fibers   W = whiskers   NA = information not available
(from Katz, 1980; Bascom, 1987b; Becher and Tiegs, 1987; Johnson and Sowman, 1987; Schoenberg, 1987)
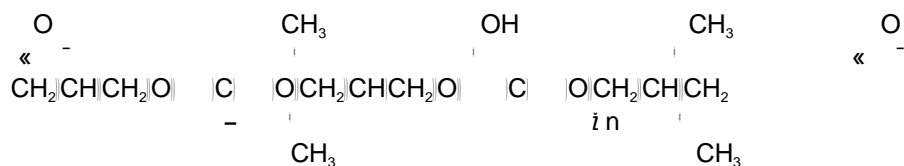
RESIN SYSTEMS

Any solid that can be processed to embed reinforcing fibers is a potential composite matrix material. Though it is impossible to discuss each resin system individually, they can be addressed as groups whose characteristics can be summarized. Chemical and physical properties of individual components are well documented and can be found elsewhere (e.g., CRC Handbook of Chemistry and Physics, latest edition; Merck Index, latest edition; IARC, 1989; SACMA, 1989; NIOSH, 1990; SACMA, 1991). Also consult the manufacturer's material safety data sheet (MSDS) for further information on the characteristics of the system as a whole.

Thermosets

The most recognizable and most widely used thermosets are the epoxy resins. They are made by reacting epichlorohydrin with a backbone chemical, usually bisphenol A or F, to produce a glycidyl group. Appropriately, the epoxies are often referred to as the glycidyl resins.

The most common epoxy is diglycidyl ether of bisphenol A or DGEBPA; the correct chemical name is 2,2-bis(p-(2,3-epoxypropoxy)phenyl)propane. The chemical formula for an epoxy follows:

$$
\begin{array}{cccccc}
O & & CH_3 & OH & CH_3 & O \\
\| & & | & & | & \| \\
CH_2CHCH_2O & C & OCH_2CHCH_2O & C & OCH_2CHCH_2 & \\
& | & & & | & \\
& CH_3 & & \text{\textit{i} n} & CH_3 &
\end{array}
$$

The molecular weight of the final epoxy can be controlled by altering the ratio of bisphenol to epichlorohydrin (Dark et. al., 1974). This is important since dermatitis has been linked with the epoxy 340 molecular weight oligomers (Fregert and Thorgeirsson, 1977; Dahlquist et. al., 1979; Bokelund et. al., 1980). Though the toxicity information will be addressed in a later section, it will be noted here that the repeat segment of the epoxy has a molecular weight of 284. For the oligomers, the molecular weights are: 340 for n=0, 624 for n=1, 908 for n=2, 1192 for n=3, etc. The resin MSDS should give the average molecular weight of the resin, as well as information on any residual epichlorohydrin.

Epoxy systems can also contain low molecular weight by-products such as di- and tri-bromophenylglycidylether, n-diglycidylphenylamine, n-glycidylphenylamine, as well as other cyclic dimers and chlorinated compounds (Dark et. al., 1974; Kowalska, 1982).

Generalized chemical reactions for the main thermosets follow (Zumwalde and Harmison, 1980; IARC, 1989; Kantz, 1989; SACMA, 1989; Thayer, 1990).

Epoxy - Most commonly a copolymer of epichlorohydrin and 2,2-bis (4-hydroxy-phenylpiperazine). Always uses a curing agent. Examples include DGEBPA (diglycidyl-ether of bisphenol A) and TGMDA (tetraglycidylether of methylene dianiline). Use temperature about 200EC. Usually have residual epichlorohydrin in the finished product.

Polyimides - Made of aromatic diamine (i.e., methylene dianiline) plus one or more acid anhydrides or esters. Bismaleimide (BMI) is the most well known resin from this group. Use temperature about 300EC.

Polyesters - Made by reacting alkylene glycol with unsaturated acids.

Phenolics - Copolymers of phenol and formaldehyde. There are two types of phenolics: (1) novalac - formed under acidic conditions, with the formaldehyde quantity insufficient to effect the polymer crosslinking, and (2) resole - usually used for prepregs. Formed under alkaline conditions with excess formaldehyde. The residual formaldehyde reacts during the cure to form methylene bridge crosslinks.

Polyurethanes - Formed by reacting diisocyanates and a polyol, polyamide, alkyd polymer or polyether polymer.

Melamine and urea formaldehydes - Made by crosslinking amino resins.

Thermoplastics

Thermoplastic resins offer a matrix material that is tougher than the thermosets, yet just as chemically resistant. Because formulation reactions do not yield rigidly crosslinked polymers, the resin's pliability can be recovered upon heating. This gives them advantages in the repair arena, but also means that they are unusable in applications where temperatures will approach the resin's softening point.

As with the thermosets, chemical and physical data on components and on the resin system should be obtained from the MSDS and other reference sources. The following information is provided as an overview (Zumwalde and Harmison, 1980; Chou et. al., 1986; ASM, 1987; Thayer, 1990):

Polyimides (can also be thermosets) - Use temperature about 315EC. Examples include (1) Ciba-Geigy's Matramid® 5218, a thermoplastic reinforced with a thermoset, (2)

Hexcel's F3900, a plastic reinforced epoxy, and (3) the Ferro Corporation CPI 2310, which is formulated without 4,4'-MDA.

Polycyanates and Benzocyclobutenes - For the most part, these resins are still in developmental stages. They are showing very high mechanical and thermal properties.

Polyphenylene Sulfide (PPS) - Used for high chemical resistivity.

Polypropylene - Tough and lightweight. Polymerization of high purity propylene gas and an organometallic catalyst.

Polyethers - Modified polysulfone polymers. Most common polyether is polyether ether ketone (PEEK). Melting temperature 334EC. Continuous use at about 250EC.

Polycarbonates - Linear polyester of carbonic acid. Highest impact resistance of any transparent plastic.

Polystyrene - Aromatic substituted linear polymer of styrene.

Polysulfone - Aromatic sulfonic acid polymer. Use temperature 190EC.

Polyarylsulfone (PAS) - Used for higher temperature resistance (275EC).

Other thermoplastics include acrylonitrile-butadiene styrene copolymer (ABS), poly-ethylenes, polypropylenes, styrene acrylonitrile polymer (SAN), polyetherimides (amorphous polymer), polyamides and polymethylmethacrylate.

High Temperature

Metal and ceramic resins provide higher temperature resistance, strength and stiffness than is possible with either the thermosets or thermoplastics. However, this is offset by the added weight and processing difficulties, particularly due to reactions between the matrix and reinforcing material.

The possible exceptions to these problems are aluminum and magnesium resins. They have maximum use temperatures - 660EC and 651EC, respectively - that well exceed that of the polymer resins, yet these metals are relatively lightweight.

The following table summarizes some of the metal matrix characteristics (Hillig, 1978; Chamis, 1981):

Metal	Density, g/cm³	Melting Point, EC	Tensile Strength, MPa	Tensile Modulus, GPa
Aluminum	2.8	580	310	70
Beryllium	1.9	1280	620	290
Copper	8.9	1080	340	120
Lead	11.3	320	20	10
Magnesium	1.74	570	280	40
Nickel	8.9	1440	760	210
Niobium	8.6	2470	280 345 @ 1200EC	100
Steel	7.8	1460	2070	210
Superalloy	8.3	1390	1100	210
Tantalum	16.6	2990	410 490 @ 1200EC	190
Tin	7.2	230	10	40
Titanium	4.4	1650	1170	110
Tungsten	19.4	3410	1520 1940 @ 1200EC	410
Zinc	6.6	390	280	70

ADVANCED COMPOSITE SYSTEMS

The information presented thus far has provided some insight into the individual components of a composite material. To get an understanding of the final product, data on the composite itself is helpful. Information on wood is shown for comparison. References

include DuPont (1978), Katz (1980), McGarry (1981), Kourtides (1985) and Chou et. al. (1986).

Fiber/Matrix	Use temp., EC	Tensile Strength, MPa	Tensile Modulus, GPa
Bulk spruce wood	--	104	10
SiC/Si	>1425	275	340
SiC/borosilicate glass	1000	--	--
C/C	2500	--	--
50% Kevlar®-50% graphite/epoxy	--	620	--
Kevlar®/epoxy	--	310	--
Fibrous glass/ epoxy	--	590	18.5
Fibrous glass/ phenolic	--	360	21.4
Graphite/BMI	--	510	106

As discussed in the section on production, a composite's characteristics are influenced by the orientation of the reinforcing fibers. The information below compares some of the differences in carbon reinforced carbon composites, based simply on different fiber alignment (Hillig, 1978):

Fiber Type/ Fiber Orientation	Weight % of Fiber	Density, g/cm³	Tensile Strength, MPa	Tensile Modulus, GPa
Low strength felt/ Random	50-60	.92-1.15	26-38	3.4-5.2
Low strength cloth/ Unidirectional	60-70	1.17-1.26	66-93	3.4-5.2
High modulus/Chopped	70-75	1.58-1.62	43-100	3.1-3.8
Low strength woven cloth/Not applicable	--	1.38-1.44	76-124	9-19
High modulus/ Unidirectional	55-60	1.63-1.69	345-524	138-172
High strength/ Unidirectional	62-65	1.47-1.49	1034-1241	152-172

FIBER MORPHOLOGY AND DEPOSITION

The concern about composite materials is mainly associated with the potential for fiber release during layup and repair operations. This scenario parallels the apprehension expressed about the man made vitreous fibers. That is, could either of these fibrous groups be responsible for respiratory damage such as that caused by asbestos?

To cause damage, fibers must first be of respirable size. Once inhaled, they must be able to reach the alveoli and be deposited. The critical factor then becomes whether the fiber can be removed by macrophage action or translocation, or if it will remain long enough and have the right chemistry or dimensions to elicit a biological response.

Many studies cite fiber diameter as the most important morphological feature of respirability (Timbrell, 1965; Stanton, 1973; Kotin, 1978; Timbrell, 1982; Hesterberg and Barrett, 1984). Fibers greater than about 5Fm will lodge in the nose; fibers 3-5Fm can enter the trachea but do not usually penetrate to the deep lung. This is due to the effective removal by the mucociliary escalator.

Fiber penetration into the deep lung occurs when diameters are less than 3Fm. This is generally accepted as the upper limit of respirability (Esmen et. al., 1978; WHO/EURO, 1985), although 3.5Fm has also been advocated (NIOSH, 1977b; IARC, 1988). Alveolar macrophages can successfully engulf fibers in this range.

Fiber respirability and retention has also been studied in relation to fiber length. The consensus is that fibers less than about 200-250Fm should be considered respirable (Timbrell, 1965; Kotin, 1978; Timbrell, 1982). However, those greater than 5Fm long are less likely to be deposited in the alveoli (Harris and Timbrell, 1977; Morgan et. al., 1980; Hammad et. al., 1982; Morgan et. al., 1982). Should a longer fiber reach the alveolar spaces, Stanton et. al. (1977; 1981) state that it has the greatest chance of causing biological activity. They showed that fibers less than 1Fm diameter and greater than 8Fm long will be most damaging. Pott et. al. (1984) agrees with this length, but suggests that the critical diameter is less than 0.25Fm.

Regardless, should long fibers reach the deep lung, macrophage translocation seems to be ineffective in removing them in significant numbers. Morgan (1980) reported that the macrophage plasma membrane is damaged when it engulfs fibers longer than 10Fm, thereby preventing removal. Fibers of this length were observed projecting outside of the macrophage, causing the cell to become "stuck" as it moved intercellularly.

In general, then, the possibility of alveolar deposition increases with decreasing fiber diameter and length. Once the fiber is permanently lodged, biological activity becomes dependent on the fiber's durability. Studies have shown that fibers in the lung get smaller,

break, undergo surface etching and become coated with gelatinous proteins over time. It is only those fibers capable of resisting such attack that may cause damage.

Scientific data on deposition, removal, dissolution and retention of composite reinforcing fibers is very limited. The exception is for fibrous glass, which has been researched as a prominent member of the man-made vitreous fiber group. Glass is thoroughly reviewed elsewhere (NAVENVIRHLTHCEN, 1990).

To evaluate alveolar macrophage effectiveness, Holt and Horne (1978) exposed guinea pigs to respirable carbon dust clouds for times varying from 7 to 24 hours. The carbon dust, obtained by hammer milling, was 98.8% nonfibrous (airborne concentration 2.9 particles per milliliter). The fibrous portion consisted of black fibers, assumed to be carbon, and transparent fibers. Nonfibrous particle size varied from submicron to "a few microns" diameter; black fibers were 1-2.5Fm diameter and #15Fm long; transparent fibers were 1.5Fm diameter x #30Fm long. When lung tissue sections were examined, the authors found that most carbon particles were intracellular in the macrophages, though the few fibers seen that were >5Fm were still extracellular at 27 weeks post exposure.

In 1982, Holt again exposed guinea pigs to mainly nonfibrous dust, but extended the exposure to 100 hours. Macrophage particulate ingestion was noted one day after exposure, with the number of dust laden macrophages increasing until about 400 days post inhalation. The number of macrophages with carbon particles gradually declined, but some were noted as long as two years later.

Hinson et. al. (1983) examined the in vivo reaction between carbon and mouse peritoneal macrophages. Test animals were given intraperitoneal injections of either carbon fibers (7-8Fm diameter x <40Fm long), chrysotile asbestos (<5Fm diameter x varying lengths) or fibrous glass (5-8Fm diameter x <40Fm long). Phagocytic response was evaluated by scanning electron microscopy at 24, 48, 120 and 144 hours. Results showed that macrophage response for all fibers progressed similarly regardless of fiber size or amount. At the 120 and 144 hour examinations, the authors reported that larger fibers of carbon and fibrous glass had been encapsulated. The study concluded that carbon fibers generated phagocytic activity comparable to that of the chrysotile, but that further evaluation was required to establish the relevance of this finding.

Deposition and clearance of Kevlar® fibers was studied by Lee et. al. (1983) following the exposure of rats to 0.1 to 18 mg/m³ of ultrafine fibers (60-70% <1Fm diameter x 10-30Fm long) for two weeks. The Kevlar® was specially prepared to simulate the ribbon-like fibrils that peel from the fibers during abrasion.

At the 3 mg/m³ and 18 mg/m³ concentrations, macrophages were rarely seen in the alveoli. At the higher concentrations, dust laden macrophages quickly accumulated in respiratory bronchioles and alveoli. Some macrophages with fibers <2Fm long were found in peribronchial lymph tissue and tracheobronchial lymph nodes at six months post

exposure. The researchers concluded that the fibers were effectively cleared by initial phagocytosis followed by transport to the lymphatic system.

The Kevlar® experiment was repeated with exposure time extended to two years and concentrations increased to as high as 400 f/cc (Lee et. al., 1988). Deposition and macrophage response patterns were similar to the previous data. At 2.5 f/cc, dust laden macrophages were almost nonexistent. At 25 f/cc, fibrils were seen in bronchioles and alveolar ducts. The 100 f/cc exposures yielded fibril deposition in alveolar duct bifurcations, bronchioles and alveoli. Macrophages were also seen in the tracheobronchial lymph nodes.

The 1988 study also noted the absence of transmigrating Kevlar® in the pleura, mesothelium or other vital organs. This phenomenon is observed after inhalation of some asbestos fibers. In addition, the number of transmigrated fibrils seen in the lymph nodes was minimal compared to that usually seen with asbestiform fibers (Lee et. al., 1981a). The authors attribute this to the fact that the curled Kevlar® fibrils tend to form aggregates, apparently preventing them from effectively penetrating the lung tissue.

ENVIRONMENTAL AND OCCUPATIONAL EXPOSURES

ENVIRONMENTAL EXPOSURES

There are no emission or hazardous waste regulations for the advanced composite materials as a whole. However, some resin components do have storage and disposal regulations. For guidance, the MSDS should be compared with the Resource Conservation and Recovery Act (RCRA) list in the Code of Federal Regulations, Title 40, Part 261. Many of the solvents are also covered, as well as resin parent chemicals and curing agents that may be present in residual amounts in cured composites.

Composite materials should never be dispose of by incineration. Fire can destroy the matrix and liberate free fibers.

Environmental air sample data for manufacturing operations is available from Henry et. al. (1982), who sampled emissions from a PAN carbon production plant.

Operation	Fibers/m³	Mass, ng/m³	Average Fiber Size, Fm
Winding operation	28	211	6.5 x 48
	60	511	6.5 x 60
	32	296	6.5 x 60
	64	908	6.5 x 50
Prepregging	24	356	6.1 x 213.1
Shuttle loom weaving	88	5497	6.7 x 749.4
Rapier weaving (down-stream of baghouse)	340	6831	3.9 x 706

OCCUPATIONAL EXPOSURES

The composite materials present a complicated exposure issue for the occupational health professional. During processing and curing, one must be concerned with the interaction of solvents, curing agents and other resin components, as well as the raw fibers. Any abrasive operation on cured materials presents the potential for fiber and dust release.

Typical composite repair operations involve cutting and sanding the damaged area, applying resin and cloth or molding the replacement piece, heat curing, sanding excess composite from the patch area, applying the finish resin coat and curing of the final coat. It is apparent why potential exposures are intertwined and complex.

Exposures to the skin and respiratory system have been documented for composites and will be discussed at length. Though not normally considered an exposure route, accidental ingestion of solvents and liquid resin components must also be considered.

There are no published reports or studies of eye irritation attributed to composite fibers, but their morphology makes them suspect for ocular problems. Kowalska (1982) notes that a common epoxy resin accelerator, borontrifluoride monoethylamine, has been linked to eye irritation. SACMA (1989) cites several solvents known to cause ocular discomfort (e.g., dimethylformamide, n-methylpyrrolidone).

An interesting, albeit peculiar, situation was investigated by NIOSH (1977a). Employees at a carbon fiber production plant (PAN precursor) reported reddening and lightening of their hair. The exact cause of the phenomenon could not be identified, though orlon by-products, settled dusts, hair and process residues were tested.

As previously stated in this document, exposures to composite chemicals are well documented elsewhere, and will be detailed here only as necessary. For a concise summary of the chemicals of concern in the advanced composite arena, consult SACMA (1989; 1991).

Research on composite fiber exposures is in its early years. Composites were not seriously used in manufacturing until the 1960s. The first studies linking the reinforcing fibers with possible health risk appeared in the late 1970s. It wasn't until the early 1980s that detailed research projects began in earnest.

Dermal

Skin irritation and sensitization by aramid fibers was evaluated by Reinhardt (1980). Volunteer panels of up to 200 people were patch tested with Nomex® and Kevlar®. They showed no potential for sensitization and minimal chance of developing irritation reactions.

Irritation and itching due to penetration of boron fibers was noted in NAVHOSP Oakland (1986). Temporary local irritation, reddening and swelling has also been associated with ceramic fibers and fibrous glass (addressed in NAVENVIRHLTHCEN, 1990). There are no published reports on irritation from the other reinforcing fibers.

The reports of composite-induced dermatitis are associated with resin components or uncured laminates. Sensitization to uncured epoxy composite was recounted by Dahlquist

et. al. (1979), who traced the problem to both the fibrous glass and to the hardener used. The authors emphasized the need to recognize that chemical penetration through the skin is aided by the fibers' mechanical irritation.

Another factor to consider is residual or unreacted chemicals in the composite. Boatman et. al. (1988) subjected graphite machining dusts to isothermal desorption and found high concentrations of 11 compounds that were of "principal concern." These included dichloroaniline, tributyl phosphate, diphenyl hydrazine and biphenyls. Dermal absorption is greatly influenced by the degree of cure, a factor that may not be addressed on the material safety data sheet. Consequently, chemical analysis of the composite should be considered when investigating dermatitis complaints.

Examples of other resin system chemicals known to cause dermatitis and/or sensitization reactions include some amine compounds (i.e., diethylenetriamine, tetraethylenepentamine), n-methylpyrrolidone, acetone, methyl ethyl ketone, methyl dianiline and epichlorohydrin (Dahlquist and Fregert, 1979; Kantz, 1989; SACMA, 1989).

Allergic contact dermatitis from epoxy resins has been traced to the 340 molecular weight oligomer through the work of Fregert and Thorgeirsson (1977). Oligomer patch tests conducted on 34 patients known to be sensitive to epoxy resin showed that all were positive for the 340 oligomer, whereas none of the subjects reacted to other oligomers up to the 1192 molecular weight. The 340 oligomer was again pinpointed as a source of dermatitis that resulted from handling uncured epoxy sign boards (Fregert et. al., 1979) and epoxy resin powder (Bokelund et. al., 1980).

Respiratory

The occupational exposure concern for the advanced composites has focused on the reinforcing fibers and whether they can be broken down enough to be respirable. Studies characterizing machining residues indicate that only carbon and Kevlar® produce such respirable particles. However, sampling results show that the fiber counts are very low for most operations. In fact, only about 3% of machining debris is fibrous - that is, has an aspect ratio $3:1 and is >5Fm long. In addition, more than 80% of these fibers are still too long or too wide to be considered detrimental (PDL, 1986; Siebert, 1987; Boatman et. al., 1988). Consequently, the primary inhalation exposure from machining operations is from particulate dusts, not fibers.

Sampling Results

Occupational exposures must be assessed by collecting air samples and quantifying the airborne fiber, dust or chemical concentration. Though the main concern is with fiber and dust exposures during composite machining, manufacturing data is included for reference when available.

When evaluating the following exposure results, keep in mind that analytical methods may not be the same for all studies. Therefore, the data presented may not be directly comparable. For example, respirable fibers are defined as having a diameter #3-3.5Fm (NIOSH, 1977a; Esmen et. al., 1978; WHO/EURO, 1985; IARC, 1988). The convention is to define a fiber as >5Fm long and having an aspect ratio $3:1 (NIOSH, 1984), but other criteria may be used (i.e., the B counting rules in NIOSH (1984)). If non-conventional criteria are used and are known, it will be noted.

Fibers

Fiber data is limited for all of the reinforcing fibers, quite unlike the abundance of such information for the man-made vitreous fibers. This is because of the relatively recent interest in the composites.

Before looking at sample results, it is important to discuss the studies characterizing the fibers and dusts generated during composite machining operations. In 1982, Mazumder et. al. evaluated dusts produced by grinding both commercially supplied laminates and virgin fiber bundles. Included for study were two each of graphite yarn, fibers and composite materials.

The study reported that laminate grindings contained fibers that were fibrillated (split), irregularly shaped and had sharp edges. The median aerodynamic diameter was 2.7Fm. Similarly, grinding raw fibers produced sharp edged fibers whose outer fibrous structure was shattered, thus generating fine particulate matter and exposing the fibers' inner core. Transverse breaks in such shatter areas decreased the mean diameter from the original 8Fm to about 4Fm.

This information was expanded by Boatman et. al. (1988), who conducted a rather thorough evaluation of five graphite prepreg composites and one fibrous glass prepreg composite. Samples were collected at the tool face during routine machining operations. The samples were sized and examined for chemical and morphological features.

The following table shows the materials included in the study, as well as dimensions of the original, non-fractionated samples. Size analysis was by light microscopy:

Composite Material, (curing agent)	Average length, Fm (range)	Average diameter, Fm	Aspect Ratio	Equip-ment[*]
Graphite/PEEK thermoplastic	38 (22-106)	10	10:1	SS
Graphite (PAN)-Kevlar®/epoxy (amine)	68 (8-340)	8	12:1	HR, SS, AS
Graphite (PAN)/ epoxy (aromatic amine)	53 (16-132)	7	11:1	HR
Graphite (pitch)/ epoxy (aromatic amine)	27 (12-61)	8	6:1	SS
Graphite (PAN)/ epoxy (amine)	29 (4-76)	7	26:1	HR
Fibrous glass/ epoxy (amine)	295 (50-624)	11	26:1	SS

[*] SS = spindle shaping - 3,450 rpm except #1 at 10,000 rpm
 HR = hand routing - 23,000 rpm
 AS = saber saw

The authors noted that the machining generated mostly particulate matter, with only an occasional fiber (aspect ratio $3:1) noted.

Using 10Fm aerodynamic equivalent diameter as the cutoff, the samples were fractionated into respirable and non-respirable. For the respirable portion, mean particle diameter was 1.7-6Fm (actual range 0.5-12.2Fm), with 74% of the overall fibers having diameters <3Fm (range 18-90%) and 86% with <5Fm diameter (range 40-96%). The ratio of respirable dust to total dust for the six samples was <1% to about 3%.

Results published by Jones et. al. (1982) and Saracco et. al. (1981) disagree with the Boatman et. al. (1988) findings that the machining dust was mostly particulate. The earlier reports found that respirable dusts generated by machining accounted for 40-70% by weight of the total dust. The difference is most likely explained by the fact that Boatman et. al. (1988) collected samples at the tool face, thereby including large particulates. Jones et. al. (1982) and Saracco et. al. (1981) assessed breathing zone samples.

Wagman et. al. (1979) reported on carbon fibers and dusts released during manufacture, handling and disposal of carbon/epoxy products. Samples were provided by Celanese, Hercules, Union Carbide, Stackpole and Great Lakes Carbon. The products varied in the degree of graphitization, surface treatment methods and fiber form (e.g., woven or chopped). Fibers in the supplied composites were 5-8Fm diameter when analyzed by scanning electron microscopy.

Dusts generated by drilling and sawing showed a combination of free fibers (50-100Fm long), resin coated fibers and free epoxy particles. The fibers from the saw samples were shorter (lengths not given) and showed some evidence of longitudinal cleaving.

A report by PDL (1986) on dusts collected from sawing and sanding graphite/epoxy composites characterizes sawing debris as mostly separated fibers and matrix fragments, whereas sanding tends to yield parallel bundles of fibers still held together by matrix. Sizing results are shown in the table below:

Operation	Diameter distribution, Fm	Length Distribution, Fm
Sawing debris	75.5% - >5.46	2-3% - 0.4-5
	99.9% - >3.44	2-3% - 5-10
		80% - 10-100
		10% - 100-200
0.1% of total dust was respirable (3.5Fm diameter cutoff)		
Sanding debris	19.3% - >5.54	<0.5% - 0.5-5
	41.2% - >3.29	<1% - 5-10
		60% - 10-50
		20% - 50-100
		5% - 100-200
		maximum length - 5000
58.8% of total dust respirable (3.5Fm diameter cutoff)		

Occupational exposure data for composite reinforcing fibers is presented in the following tables. The data is separated by fiber for clarity and ease of comparison, both within a

particular fiber and between different fibers. Unless otherwise noted, samples are personal breathing zone.

Operation/Location	Results[*] (range)	Reference/Comments[*]
CARBON/GRAPHITE		
Fabrication plant - general area		Henry et. al. (1982)
	0.0008 f/cc 0.0021 mg/m³	fiber size - 6.6Fm d x 30.9Fm l
USSR PAN plant - all general area		Fedyakina (1982)
Fiber forming - oven insertion & removal	Avg. 1.15 mg/m³ (0.3-7.5)	120 samples
Fiber forming - oven unloading & cleaning	Avg. 25.21 mg/m³ (0.1-97.0)	44 samples. Size: 89.6% <2Fm d; 98.8% <5Fm d
Fiber processing: winding	Avg. 6.46 mg/m³ (0.1-14.0)	20 samples
weaving	Avg. 2.1 mg/m³ (0.1-18.3)	81 samples
trimming	Avg. 6.6 mg/m³ (0.1-18.0)	20 samples. Size: 84.7% <2Fm d; 96.5% <5Fm d
Continuous filament PAN plant		Jones et. al. (1982)
Cutting, grinding, milling	0.39 mg/m³ ± .31, T 0.16 mg/m³ ± .09, R	Mostly non-carbon and non-fibrous. 7 samples. Size: 0.5-7Fm d
Winding	0.19 mg/m³ ± .17, T 0.07 mg/m³ ± .05, R	5 samples. Size: 8-10Fm d
Production	0.08 mg/m³ ± .03, T 0.03 mg/m³ ± .01, R	26 samples. Size: 8-10Fm d
NARF, Cherry Point		NAVHOSP Cherry Point (1986)
Sanding carbon/epoxy patch	1.49 mg/m³, T (TWA)	436 minute sample
NAS, Lemoore AIMD		NAVHOSP Lemoore (1984)
Routing FA-18 carbon flaps	1.4 mg/m³, T (TWA 0.36 mg/m³)	122 minute sample
	0.7 mg/m³, T (TWA 0.18 mg/m³)	122 minute sample
General area sample	0.3 mg/m³, T (TWA 0.08 mg/m³)	126 minute sample
	0.2 mg/m³, T (TWA 0.05 mg/m³)	125 minute sample

Operation/Location	Results[*] (range)	Reference/Comments
NAS, Lemoore AIMD		NAVHOSP Lemoore (1986)
Pneumatic sanding, FA-18 carbon/ epoxy patch	0.32 mg/m³, T (TWA 0.11 mg/m³)	160 minute sample
General area sample	0.13 mg/m³, T	158 minute sample
MCAS, Beaufort		NAVHOSP Beaufort (1986)
FA-18, graphite/epoxy	0.107 mg/m³, T (TWA) 0.37 mg/m³, R (TWA)	
FIBROUS GLASS		
NARF, Cherry Point		NAVHOSP Cherry Point (1986)
Sanding patches	1.02 mg/m³, T (TWA)	430 minute sample
NARF, Norfolk		NAVMEDCLINIC Norfolk (1985)
Sanding engine door & radome	0.71 f/cc ± .21, T (TWA 0.43 f/cc)	227 minute sample
Sanding small parts	0.31 f/cc ± .20, T (TWA 0.25 f/cc)	222 minute sample
	0.94 f/cc ± .20, T (TWA 0.58 f/cc)	243 minute sample
	1.85 f/cc ± .29, T (TWA 0.73 f/cc)	164 minute sample
Grinding F-14 ventral fin	0.32 f/cc ± .13, T (TWA 0.37 f/cc)	395 minute sample
Grinding 2 fairings	<0.083 f/cc, T (TWA <0.10 f/cc)	60 minute sample
Grinding A-6 radome	1.19 f/cc ± .16, T (TWA 0.87 f/cc)	310 minute sample
Fort Eustis, VA		USAEHA (1991)
Helicopter rotary & wing repair, UH60A and EH60A	0.83, 0.89, 0.63, 0.89, 0.21, 0.47, 0.35, 0.53 f/cc	trimming damage, preparing patch, patching, hand sanding and priming patch
General area sample	1.36, 0.53 f/cc	
External fuel tank repair, fibrous glass patch on Kevlar® tank	0.85, 17.62 f/cc	hand sanding, 50 grit disc sanding
	3.63 f/cc	100 grit disc sanding
	6.17 f/cc	routing damaged area
	237.87 f/cc	router cutting

[*] T = total   R = respirable   TWA = 8 hour time weighted average

Operation/Location	Results[*] (range)	Reference/Comments
Prepreg FG/phenol formaldehyde repair - sample location not given		Breysse (1989)
	0.48 - 1.1 mg/m³, T	SEM analysis
ARAMID		
PPD-T plant		Reinhardt (1985a; 1985b) P&CAM 239 analysis
Polymer spinning - general area	ND ND-0.01 f/cc	4 samples 5 samples
Yarn testing - general area	ND	2 samples
Yarn rewinding - general area	ND	4 samples
Yarn handling - general area	ND-0.01 f/cc ND-0.06 f/cc ND-0.01 f/cc	5 samples 4 samples 3 samples
Fiber cutting - sample location not given	Avg. 0.2-0.33 f/cc (Maximum 0.44 f/cc)	4 samples, 6 hr. operation NIOSH 7400, P&CAM 239 analysis
	Avg. 0.01-0.03 f/cc (Maximum 0.04 f/cc)	7 samples, 3-4 hour operation
	Avg. 0.02-0.08 f/cc (Maximum 0.44 f/cc)	5 samples, 20-50 minute operation
	Avg. 0.01-0.02 f/cc (Maximum 0.05 f/cc)	10 samples, 3-6 hour operation
	Avg. 0.01 f/cc (Maximum 0.02 f/cc)	8 samples, 2-5 hour operation
Pulp making - sample location not given	Avg. 0.02-0.25 f/cc (Maximum 0.28 f/cc)	14 samples, 2-4 hour operation
	Avg. 0.02-0.17 f/cc (Maximum 0.30 f/cc)	6 samples, 80 minutes operation
	Avg. ND-0.03 f/cc (Maximum 0.09 f/cc)	5 samples, 1.5-4 hour operation
Customer plant - sample location not given	Avg. 0.01-0.04 f/cc (Maximum 0.05 f/cc)	11 samples, 4-7 hour operation
	Avg. 0.01-0.03 f/cc) (Maximum 0.07 f/cc)	6 samples, 1.5-3.5 hour operation
Gasket plant, compressed sheeting - sample location not given	Avg. 0.01-0.02 f/cc (Maximum 0.04 f/cc)	3 samples, 8 hour operation
	0.09 f/cc	2 samples, 3-4 hour operation

[*] T = total   ND = none detected   Avg. = average

Operation/Location	Results[*] (range)	Reference/Comments
Kevlar® plant		DuPont (1986)
Cutting, carding	0.02-0.4 f/cc, R	
Pulp handling	0.1-0.2 f/cc, R	
MISCELLANEOUS FIBERS		
Silicon carbide production		Bye et. al. (1985). Results are range of geometric means. Only fibers with $10:1 aspect ratio counted.
Mixing raw material	0.3 f/cc	1 sample
	0.1-1.9 f/cc	7 samples
	1.8-4.9 f/cc	4 samples
Furnace operation	0-3.6 f/cc	16 samples
	0.1-1.9 f/cc	4 samples
	0.1-0.7 f/cc	7 samples
Raw product separation	0.2-0.7 f/cc	6 samples
	0.2-2.7 f/cc	6 samples
	0.2 f/cc	3 samples
Preparation of final product	0-0.1 f/cc	2 samples
	0.1-0.2 f/cc	3 samples
	0-0.1 f/cc	3 samples
Note: For all fibers: 80% <0.5 d x 75Fm l. Maximum length 100Fm. Range of geometric mean sizes = 0.5-2.5Fm d x 1-50Fm l.		
NARF, Cherry Point		NAVHOSP Cherry Point (1986)
Titanium repair operations: AV-8B sanding/filling	<0.016 f/cc (TWA)	392 minute sample
	<0.017 f/cc (TWA)	388 minute sample
	<0.017 f/cc (TWA)	386 minute sample
Grinding/filing	<0.017 f/cc (TWA) 0.294 mg/m³, T (TWA)	392 minute sample
Cutting with hacksaw/filing	0.49 mg/m³, T (TWA) 1.31 mg/m³, T (TWA)	388 minute sample

[*] T = total   R = respirable   d = diameter   l = length   TWA = 8 hour time weighted average

Resin Systems/Cleaning Solvents

Occupational exposures to resin system components and cleaning solvents can occur during resin mixing, curing and repair cleaning. A few studies have also assessed airborne levels of chemicals generated during machining operations, and bulk dust analysis is also available.

It is appropriate to note here that exothermic reactions, known as exotherms (unintentional runaway or out-of-control chemical reactions), can occur with hot melt or solution resins and with preimpregnated resin materials. The reaction is marked by a rapid uncontrolled rise in temperature that can generate potentially dangerous vapors and mists. Smoke and fumes emitted during advanced stages can also contain toxic products.

Boatman et. al. (1988) performed thermal gravimetric analysis of graphite and fibrous glass dusts generated during machining operations. Gas chromatography/mass spectrophotometry analysis of the offgassing (heating temperatures from ambient to 860EC) identified the "high concern compounds" listed below. There was negligible offgassing at <250EC.

  fibrous glass - dichloroaniline, triphenylphosphine oxide
  PAN graphite - dichloroaniline, tributylphosphate, benzothiazole, dibenzofuran amine,
    diphenylphosphine oxide
  Pitch graphite - no compounds of concern

A bulk and a machining dust carbon composite sample were analyzed by high pressure liquid chromatography/ultraviolet detector for polycyclic aromatic hydrocarbons (PAH) (Clayton Environmental Consultants, 1986, 1987). The bulk sample had less than detectable levels of PAH, but the dust sample yielded the following results (Fg/g):

  acenaphthylene - maximum level detected = 220
  phenanthrene - 36
  anthracene - 1.8
  fluoranthene - 8.3
  benzo(a)anthracene - 2.8
  chrysene - 2.2
  benzo(b)fluoranthene - 1.1
  benzo(k)fluoranthene - 1.2
  benzo(a)pyrene - 1.2
  dibenzo(a,h)anthracene - 4

Kowalska (1982) evaluated dusts from carbon/epoxy composites drilling. Analysis revealed 1% weight/weight (w/w) volatile compounds. The actual compounds identified in the dusts were:

Hercules 3501 - water, p-propylaniline, methyl ethyl ketone, propioamide, 4,4'-diamino-diphenylsulfone (DDS), methyl DDS, dimethyl DDS, trimethyl DDS, tetramethyl DDS, 1,4-diaminobenzene

Ciba-Geigy Fibreduk 914C - water, triglycidyl p-aminophenol, 4,4'-diaminodiphenylmethane, methyl ethyl hexene

The author's interpretation is that the hazardous chemicals are probably retained in the reinforcing materials as well as being present in the matrix particulate. However, the chemical amounts detected were so minute that extra caution would be advocated only for hypersensitive personnel.

Sampling data for resins and solvents during actual repair operations was found in only two reports. The information is summarized in the following table. Unless otherwise noted, results are personal breathing zone.

Operation/Chemical	Results, ppm (8 hr. TWA)	Results, mg/m³ (8 hr. TWA)
USAEHA (1991). Rotor wing repair:		
Patch cleaning - acetone	<6.6, <6.6, <7.0	
	general area - <6.9	
Patch cleaning - epichlorohydrin	<0.8, <0.5, <0.4, <0.8, <0.1, <0.8	
	general area - <0.7	
NAVMEDCLINIC Norfolk (1985)		
Mix, laminate, apply epoxy-epichlorohydrin		0.1 (0.02) 0.09 (0.02) 0.06 (0.01) 2.8 (0.35) 0.1 (0.003)
Glazing (final epoxy coat)-epichlorohydrin		0.2 (0.06)
Layup with EPON 828:		
acetone	0.82 (0.67)	
xylene	0.20 (0.16)	
MEK	<0.04 (<0.03)	
Mix & apply EA956:		
acetone	<0.32 (<0.04)	
xylene	0.77 (0.11)	
MEK	<0.26 (<0.04)	

COMPOSITES IN FIRES

The extensive use of composites on aircraft presents a somewhat unique exposure scenario should there be a mishap involving a crash, fire and/or explosion. A crash or explosion can damage the composite and expose or liberate fibers. The main concern with fire is the possibility that the fibers, liberated as the resin burns off, will splinter to a smaller size. This may not only make them respirable, but enhances the chance that they will be translocated by wind or by the force of any explosion. Additional problems can come from the pyrolysis products of the burning resins. The crash presents a potential environmental exposure, as well as exposures to firefighters, accident investigators and site cleanup personnel.

Several experimental studies have been done to assess and define composite combustion products. When studying smoke emissions from burning graphite/epoxy and graphite/bismaleimide (BMI), Kanakia et. al. (1980) reported that the only constituent of significance was carbon monoxide (CO). However, the epoxy sample did produce hydrogen cyanide at 10 watts per square centimeter (W/cm²), suggesting that this could be a problem in intense fires that produce a lot of smoke. Also, the epoxy composite had a tendency to auto-ignite around 7 W/cm², and generated 23% more heat and 42% more CO than did the BMI sample.

In a similar project using graphite/epoxy composites, Kubin (1979) identified the principle combustion products as water, carbon dioxide and carbon monoxide. Additional chemicals included ethane, propane, isopropyl alcohol, benzene and trace amounts of propylene.

Kourtides (1985) studied the thermal properties of graphite reinforced vinylpoly-styrylpyridine/bismaleimide (VPSP/BMI). This resin was reportedly a newly developed formulation undergoing study because of its greatly increased fire resistance over conventional resins. The VPSP/BMI exhibited a 500% decrease in smoke evolution, 45% increase in thermal stability and 300% decrease in mass loss at 5 W/cm² when compared with glass/epoxy panels. Though this could make a significant difference during aircraft mishaps, the VPSP/BMI system does not appear again in the literature.

Available laboratory evidence indicates that burning resins do not pose any additional hazard beyond that normally encountered during a fire. The only chemical sample data found for an aircraft crash is the polyaromatic hydrocarbon analysis from post-fire bulk analysis on graphite/epoxy (NAVENVIRHLTHCEN, 1987). The only compound found, present in three of the four samples, was acenaphthylene. It was speculated that this was from the JP5 fuel. Results for the other compounds (listed below) were less than the level of detection. Results for the unburned carbon composite bulk control sample were also below detectable levels for all compounds.

Naphthalene	Benzo(a)pyrene
Acenapthene	Benzo(b)fluoranthene
Fluorene	Benzo(k)fluoranthene
Phenanthrene	Benzo(a)anthracene
Chrysene	Dibenzo(a,h)anthracene
Anthracene	Benzo(q,h,i)perylene
Fluoranthene	Indeno(1,2,3,c,d)pyrene
Pyrene	

In contrast, there is much data on fiber concentrations during burning and cleanup of composite materials. When composites burn, the matrix generally ignites and decomposes, thus exposing the fibers. Should there be any agitation, as during a crash or explosion, the fibers easily fragment and become airborne. The subsequent disturbance of the uncoated fibers as investigation and cleanup begins presents an even greater concern because of the personnel on site. Keep in mind that if the resin is intact, the fibers are relatively heavy and less likely to become airborne.

Mazumder (1982) heated raw carbon fibers at 850EC, then examined them using scanning electron microscopy (SEM). He found that the fibers did indeed fragment during oxidation, decreasing the diameter. Mazumder also heated a carbon/epoxy composite, finding that the epoxy completely burned off the fibers at temperatures above 400EC, with the first fiber structural changes occurring after about 30 minutes of heating. However, the resultant debris was mostly amorphous particulate matter.

Wagman et. al. (1979) reports a similar experiment. SEM analysis of the burn residues showed that uncoated carbon fibers first began to dimple and thin after one minute at 1000EC. Pitting was deep and extensive after 3.5 minutes. When carbon fibers embedded in an epoxy resin were incinerated, fiber degradation was delayed, showing almost no damage after 5 minutes. For carbon woven cloth, it took 23 minutes at 1000EC before the fibers first showed structural changes.

The most comprehensive summary of experiments to characterize fiber release during aircraft mishaps was reported by NASA (1980)[*]. Studies were designed to evaluate fiber size, dispersion patterns, release rates and resuspension potential.

[*] Note: This report summarizes numerous individual experiments designed and coordinated by NASA. Many of the projects were sponsored by the U. S. Navy and the U. S. Army.

In one experimental scenario, composite structural components were burned outside to simulate an aircraft fire. Air samples were collected above the flames and at several areas downwind. Over 1300 samples were collected 140 meters downwind to characterize fiber dissemination patterns. The fibers fell into the following categories:

Category	Description	Size	Fall Rate, cm/sec	Dispersion Range
Single fiber	self explanatory	3-8Fm diameter, 0.1-15 mm long	2	0 to >100 km
Cluster	hundreds of fibers clumped together	--	10-20	0 to 10 km
Strips	single lamina bound together by incompletely burned resin or by char	0.15 mm diameter, varying length and width	100-500	0-2 km
Impact fragment	multiple laminate pieces	variable	--	immediate crash site
Unrecovered	fibers >1 mm long, consumed fibers and epoxy	--	--	--

Another test scenario involved large scale aviation jet fuel fire tests designed to characterize the composite debris. In general, results showed that the epoxy matrix (about 30% of the original test mass) was consumed in the fire. Single fibers accounted for only 0.2-0.6% of the original fiber mass, the remainder being released as either clumps, fragments or particulate. Only when explosives were used did single fibers released exceed 1% of the original mass (up to 3.5%).

Fiber release rates during fires were evaluated by using active sensors placed on Jacob's ladders downwind of burning composites. Researchers found that single fiber release is essentially constant throughout the fire, with cumulative values of:

2 minutes after fire begins - 0 fibers (no release yet)
12 minutes after fire begins - 30,000 f/m²
16 minutes after fire begins - 47,000 f/m²
20 minutes after fire begins - 55,000 f/m²

Released fiber dimension was dependent on the test conditions - that is, with or without agitation and inside versus outside. Following is a summary of the data from seven outdoor tests. The average diameter of the original material was 7Fm. The mean post-burn diameter was 4-4.7Fm.

Fibers > 1 mm long - 19-38% 3-4Fm diameter
                    23-43% 4-5Fm diameter

  (most fibers were reported as 1-3 mm diameter)

Fibers < 1 mm long - accounted for 67-74 mass % of total single fibers released with
  fire only, and up to 98% of fibers released with fire and explosion

Respirable fibers (<3Fm diameter x <80Fm long, 3:1 to 10:1 aspect ratio) accounted   for
<23% of total fibers released; average fiber size 1.5Fm diameter x 30Fm long

Lastly, to monitor potential resuspension rates, cut carbon fibers were deposited in an uninhabited desert area. The area was monitored at regular intervals for over three years. Less than 1% of the original fiber mass was resuspended during the test period. Interestingly, average fiber lengths decreased during the evaluation period, from the original 9 mm length to 1.8 mm after six months and 1.7 mm at three years.

Air samples collected at actual mishap sites are summarized in the following tables. All samples are personal breathing zone unless otherwise noted. Cassette fiber counts are included when availble (fibers have been detected on collection cassette walls and caps and on cowl walls. This is addressed in the section on sampling and analysis).

Samples with Cassette Fiber Counts (8 hour TWA includes cassette fiber counts)

Sampling Description	Filter Results, f/cc	Cassette Results, f/cc	TWA, f/cc	Reference, Comments, Gravimetric Results
AV-8B post crash engine removal. Prying, sawing, pounding frame - graphite	1 - 0.002 2 - 0.003 3 - 0.002	1 - 0.026 2 - 0.036 3 - 0.017	1 - 0.016 2 - 0.022 3 - 0.011	Particle Data Labs (1987a; 1987b); NAVENVIRHLTHCEN (1987) Counted graphite fibers only.
Fiber Length, Fm	1 - 10-15% @ 5-25; 1-2% @ 25-50; 20% @ 50-100; 40-50% @ 100-300; 10% >300			
	2 - 5% @ 5-25; 20% @ 25-50; 30% @ 50-100; 30% @ 100-300; 15% @ >300			
	3 - <1% @ 5-25; 1-2% @ 25-50; 10% @ 50-100; 50-60% @ 100-300; 5% >300			
Fiber Diameter, Fm	For all samples, #2% were 0.2-2. Rest of fibers >2.			
AV-8B cleanup - graphite				NAVENVIRHLTHCEN (1987). Burn duration . 5 minutes.
Sweeping runway	0.048 0.033	0.019 0.013	0.020 0.012	143 minute sample (30% fibrils) 143 minute sample (30% fibrils)
Crane operator righting fuselage	0.012	0.005	0.004	125 minute sample (1-2% fibrils)
Removal of components from aircraft	0.058	0.023	0.030	175 minute sample (30% fibrils)
Area perimeter removal	0.023	0.009	0.0098	147 minute sample (1-2% fibrils)
Removal downwind	0.010	0.001	0.035	147 minute sample
Removal under wreckage; downwind work	0.075	0.025	0.029	140 minute sample (25% fibrils)

| Digging in wreckage | 0.087 | 0.033 | 0.060 | 238 minute sample (20% fibrils) |

Samples with Cassette Fiber Counts (8 hour TWA includes cassette fiber counts), continued

Sampling Description	Filter Results, f/cc	Cassette Results, f/cc	TWA, f/cc	Reference, Comments, Gravimetric Results[*]
Excavating soil	0.14 0.007	0.056 0.084	0.097 0.039	238 minute sample (15% fibrils) 238 minute sample (20% fibrils)
Active component removal				<0.47 mg/m³(TWA - <0.10 mg/³) <0.22 mg/m³(TWA - <0.11 mg/m³) <0.39 mg/m³(TWA - <0.169 mg/m³)
General area, downwind	0.012	0.001		130 minute sample
Fiber dimensions:	Diameter: 1-20Fm (minimum diameter seen = 0.5Fm). Length: 5-100Fm.			

Samples without Cassette Fiber Counts

Sample Description	Filter Results, f/cc	TWA, f/cc	Reference, Comments, Gravimetric Results[*]
FA18 crash in desert. Carbon.			Mahar (1990). Apparent complete combustion of epoxy matrix. Wreckage sprayed with fixative.
10 meters E of impact		<0.01	0.03 mg/m³, T; 0.02 mg/m³, R
10 meters W of impact			0.03 mg/m³, T
45 meters SW of impact			0.09 mg/m³, T
2 days post crash clean-up		<0.06	0.47 mg/m³, 24.1 mg/m³, T (TWA) (mishap investigator)
6 days post crash: earth mover burying debris		<0.04	18.3 mg/m³, T (TWA) (0.5Fm d x 10 Fm l)
6 days post crash: earth mover assistant		0.56	15.9 mg/m³, T (TWA) (2Fm d x 7-8Fm l)
6 days post crash - 40 meters W of impact		<0.02	<0.18 mg/m³, T
AV-8B Harrier II			Formisano (1989). Analysis notation: fibers seen on cassette walls but not counted.
2 days post crash:	<0.016	<0.005	151 minute sample
Hand searching debris	6.142 3.670	0.345 0.206	27 minute sample 27 minute sample
Forklift operator	2.865	0.161	27 minute sample

* T = total   R = respirable   d = diameter   l = length

Samples without Cassette Fiber Counts, continued

Sampling Description	Filter Results, f/cc	TWA, f/cc	Reference, Comments, Gravimetric Results
Equipment operator	<0.030	<0.005	76 minute sample
Guiding operator	<0.073	<0.005	34 minute sample
Loading debris in truck	6.998	0.306	34 minute sample
3 day post crash: pick- ing up debris by hand	<0.671	0.161	115 minute sample
4 day post crash: work- in impact crater	0.584	0.026	21 minute sample
4 day post crash: moving wing	0.363 3.170	0.014 0.066	19 minute sample 10 minute sample
General area samples:			
1 day post crash: tail section	<0.010 <0.011		256 minute sample 219 minute sample
1 day post: main debris, south	<0.009 0.015		272 minute sample 206 minute sample
1 day post: main debris, east	0.015 <0.013		166 minute sample 192 minute sample
1 day post: main debris, west	0.008		349 minute sample
1 day post: impact crater	<0.010 <0.010		235 minute sample 228 minute sample

Samples without Cassette Fiber Counts, continued

Sampling Description	Filter Results, f/cc	TWA, f/cc	Reference, Comments, Gravimetric Results
2 day post: impact crater	0.018 <0.015		134 minute sample 160 minute sample
2 day post: near wing	<0.018 1.060		132 minute sample (searching debris by hand) 221 minute sample
2 day post: main debris, north	<0.066		36 minute sample
2 day post: main debris, south	0.118		210 minute sample (hand searching)
3 day post: impact crater	<0.043 1.835		57 minute sample 56 minute sample
3 day post: main debris, north	<0.048		62 minute sample
3 day post: near stacked debris	0.692		89 minute sample
3 day post: moving tail section	0.694		42 minute sample
4 day post: near stacked debris	0.020		217 minute sample
F14 salvage operation - boron			NAVHOSP Oakland (1986). Crash area periodically sprayed with water.
Crane operator		0.02	176 minute sample
Crash pit		0.02 0.06	111 minute sample - 3.1 mg/m³ (69 minutes) 111 minute sample - 2.5 mg/m³ (61 minutes)
Crash pit - general area		0.06 0.02	115 minute sample - 4.3 mg/m³ (71 minutes) 69 minute sample

| Fiber Dimensions | "Majority" 1-2Fm diameter x 7-60Fm long |

The only other exposure data available on aircraft mishaps is for fiber penetration. NAVHOSP Oakland (1986) reported boron fibers in the hands and feet of personnel cleaning an F14 (boron/epoxy) crash site. Boron slivers were found in the palms of those handling debris, despite the fact that they were wearing leather gloves. Six people also had fibers in the soles of their feet (footwear not specified). Fibers were found lodged in the boot soles of other cleanup personnel.

Because carbon fibers are conductive, released fibers can short circuit electrical equipment. This issue has been addressed mostly in relation to aircraft mishaps, since there is potential for fiber release and subsequent fiber translocation to surrounding equipment.

NASA (1980) summarized numerous laboratory studies on electrical device failure during and after exposure to carbon fibers. Low voltage equipment (0-15 volts) was susceptible to failure if the fibers could reach the circuitry. Moderate voltage (15-220 volts) devices burned most of the fibers before they could cause damage. Similarly, high voltage (440 volts) equipment exhibited no adverse effects from fiber exposure. Equipment operating at >440 volts did undergo flashover when exposed to "long" fibers (average 9 mm). Fibers sized at 2 and 4.3 mm did not elicit flashover, even at exposures of $>10^7$ fiber-sec/m³.

Margulies and Zasada (1981) summarized Department of Defense reports on aircraft accidents, and reported that the amount of carbon released during a single mishap does not pose a threat to electrical equipment in the vicinity. The report stated that the crash site should be properly contained (i.e., sprayed with fixatives, keep disturbance to a minimum) to ensure that surrounding electrical equipment is not affected by the fiber release. Margulies and Zasada (1981) and Conner (1981) also point out that concerns about electronic failures could be more of an issue in the future as the percentage of composites used on aircraft continues to increase.

REGULATORY STANDARDS AND CURRENT RECOMMENDATIONS

Fibers/Dusts

The current Navy Occupational Safety and Health (NAVOSH) standards for composite reinforcing materials are given below. They are currently all regulated as dusts. Unless otherwise noted, all values represent 8 hour time weighted averages. Listed in parentheses is the source and year for the standard, obtained using the hierarchy in OPNAVINST 5100.23B, Chapter 16, paragraph 16004.

Graphite, natural [7782-42-5]	2.5 mg/m³, respirable (OSHA, 1989)
Graphite, synthetic [7782-42-5]	10 mg/m³, total (OSHA, 1989)
	5 mg/m³, respirable
Carbon[*] [7440-44-0]	15 mg/m³, total (OSHA, 1989)
	5 mg/m³, respirable
Aromatic polyamides[*]	15 mg/m³, total (OSHA, 1989)
	5 mg/m³, respirable
(i.e., Kevlar® [26125-61-1])	
Fibrous glass (dust) [65997-17-3]	10 mg/m³ (ACGIH, 1978)
Metals, not otherwise regulated[*]	15 mg/m³, total (OSHA, 1989)
	5 mg/m³, respirable
Aluminum (as Al) [7429-90-5]	15 mg/m³, total (OSHA, 1989)
	5 mg/m³, respirable
Beryllium (as Be) [7440-41-7]	0.002 mg/m³ (OSHA, 1970)
	0.005 mg/m³, STEL
	0.025 mg/m³, Ceiling (30 minutes)
Tungsten (as W) [7440-33-7]	5 mg/m³ (OSHA, 1989)
	10 mg/m³, STEL
Copper (dust, as Cu) [7440-50-8]	1 mg/m³ (OSHA, 1989)
Molybdenum (as Mo) [7439-98-7]	10 mg/m³, total (OSHA, 1989)
Tantalum, metal dust [7440-25-7]	5 mg/m³, (OSHA, 1989)
Ceramics, not otherwise regulated[*]	15 mg/m³, total (OSHA, 1989)
	5 mg/m³, respirable
Aluminum oxide [1344-28-1]	10 mg/m³, total (OSHA, 1989)
	5 mg/m³, respirable
Boron oxide [1303-86-2]	10 mg/m³, total (OSHA, 1989)

Calcium oxide [1305-78-8]	5 mg/m³ (OSHA, 1989)
Silicon carbide [409-21-2]	10 mg/m³, total (OSHA, 1989)
	5 mg/m³, respirable
Specialty reinforcements[*]	15 mg/m³, total (OSHA, 1989)
	5 mg/m³, respirable

[*] Denotes fibers/dusts not specifically regulated. Consequently, they fall under the OSHA PEL for "Particulates not otherwise regulated."

Note that these PELs are based on "pure product" exposures. They do not account for additives or residual resin compounds.

These standards apply at all Navy facilities unless more strict recommendations are made by the manufacturer's MSDS. Should this occur, consult the cognizant industrial hygienist or the Navy Environmental Health Center to assess the suggested exposure limit based on its scientific validity. Manufacturers typically offer recommended exposure limits (REL) in fibers per cubic centimeter (f/cc). For example, Carborundum (1991) recommends a 1 f/cc limit for carbon.

Always consult the manufacturer's MSDS for the individual fiber, resin, solvent, or for the composite system. Should other chemicals be present, any applicable PELs for regulated chemicals must also be met.

Other Classifications

IARC (1988) classifies glass filaments as Group 3, not classifiable as to carcinogenicity to humans. Ceramic fibers fall under Group 2B, possibly carcinogenic to humans. These assessments were made during the International Agency for Research on Cancer (IARC) studies of man-made mineral fibers.

The latest National Toxicology Program report (NTP, 1989) does not list any of the composite reinforcing materials.

In an Environmental Protection Agency (EPA) health hazard review of non-asbestos fibers, Vu (1988) recommends that aramid fibers be classed as Group 2B, possibly carcinogenic to humans. This is based on EPA policy that any material producing tumors in animals be classed as a minimum Group 2B. This is without regard to exposure method, type of tumor or number of animals developing tumors.

Resins/Solvents

   Resin components and solvents must be looked up individually for the applicable PEL. Examples of a few commonly used chemicals follow:

Epichlorohydrin [106-98-8]
     PEL: 2 ppm (18 mg/m³)
     IARC (1987): Group 2A, probably carcinogenic to humans
     NTP (1989): Reasonably anticipated to be carcinogenic

DGEBPA [1675-54-3]
     IARC (1989): Group 3, not classifiable for carcinogenicity to humans

Phenyl glycidyl ether
     IARC (1989): Group 2B, possibly carcinogenic to humans

Formaldehyde [50-00-0]
     PEL: 1 ppm
     STEL: 2 ppm (15 minutes)
     IARC (1987): Group 2A, probably carcinogenic to humans
     NTP (1989): Reasonably anticipated to be carcinogenic

Styrene monomer [100-42-5]
     PEL: 50 ppm (215 mg/m³)
     STEL: 100 ppm (425 mg/m³)
     IARC (1987): Group 2B, possibly carcinogenic to humans

4,4'-methylene dianiline [101-77-9]
     PEL: 0.1 ppm (0.81 mg/m³)
     IARC (1987): Group 2B, possibly carcinogenic to humans
     NTP (1989): Reasonably anticipated to be carcinogenic

SAMPLING AND ANALYSIS

FIBERS

The sampling strategy for reinforcing fibers will depend on the standard or recommended exposure limit being followed. Though NAVOSH standards are currently gravimetric, many manufacturers use fiber counts for their recommended exposure limits.

Gravimetric

Air samples for all composite dusts can be collected using methods 0500 and 0600 in the NIOSH manual of analytical methods (NIOSH, 1984). These methods provide the sampling and analysis criteria for total and respirable dusts, respectively. The individual procedures list the sampling protocol, measurement techniques and method accuracy data. Since the respirable fraction is the one of interest, it is the recommended sampling protocol.

The main objection to using gravimetric methods is that all dust in the sample area is collected. Without additional evaluation of the filter (i.e., by scanning electron microscopy or transmission electron microscopy), there is no way to identify whether the total weight of the dust is truly reflective of the particular contaminant being sampled.

Fiber Counting

Airborne fiber samples can be collected and analyzed with method 7400 from the NIOSH manual of analytical methods. As of this writing, the most current procedure is revision 3 of 15 May 1989. Samples are collected on 25 mm cellulose ester filters using a conductive cowl, the filter is cleared, and phase microscopy is used for filter counting. There are two sets of counting rules: (1) the A rules stipulate that only fibers >5Fm long and with an aspect ratio (length to width ratio) $3:1 will be counted; (2) the B rules define a fiber as both >5Fm long and <3Fm in diameter. The aspect ratio must be $5:1. The B rules count fiber ends rather than individual fibers. Results should always specify which rules were used.

Analytical reports on several air samples collected during composite repair operations note the presence of fibers on the cassette and cowl walls and on the cassette cap. PDL (1987a; 1987b) comments that fiber counts done on the rinsed cassettes were higher than those from the filter alone. This appears to be a particular problem with carbon and graphite because of their electrostatic charge.

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It has been suggested that carbon and graphite air samples collected by method 7400 include cassette rinsing during analysis (PDL, 1987a, 1987b; Silverberg, 1987). A recommended procedure is to coat the cowl and cassette walls and cap with an aqueous solution of polyvinyl alcohol. After drying, the film containing embedded fibers can be removed and counted.

PDL (1987a) examined both the sample filters and the films obtained by the above procedure after sampling for graphite. They found that the fibers on the films were mostly graphite, whereas filters contained only about half graphite:

Graphite fibers, housing (f/cc)	Total f/cc on filter	Graphite f/cc on filter
0.026	0.004	0.002
0.036	0.006	0.003
0.017	0.005	0.002

It should be noted that several studies collected and analyzed side-by-side comparisons of gravimetric and fiber counting methods (Corn and Sansone, 1974; Esmen et. al., 1979; Friar and Phillips, 1989). Without fail, the data showed that there is no correlation between results obtained by the two procedures. Fiber counts can not be reliably estimated from gravimetric analyses, nor does weight give any indication of the number of fibers present.

Automated

There are some automated monitors and alternative analytical methods that have been researched for use with carbon and graphite measurements. Conner (1981) evaluated 27 methods, some experimental, for identification and counting of carbon. Some examples include magnetic alignment, spark spectrometry, angular light scattering and photothermal detection/electric alignment. He concluded that none of the instruments was capable of identification and measurement of carbon when other fibrous material was present.

Peters et. al. (1981) evaluated instrumentation capable of monitoring carbon fibers during emission, manufacturing, use and disposal scenarios. He recommends further testing and refinement of such techniques as electric grid-arc, optical opacity (total carbon only) and rotating lens optical scattering. The study also concluded that the sampling instrument would have to be somewhat specific for the monitoring site.

RESIN COMPONENTS AND SOLVENTS

Sampling for resin components and solvents will be dependent on what compounds are being used. For guidance on required sampling media, flow rates, special instructions and analytical method, consult NAVENVIRHLTHCEN (1991). Some common resin components that could be sampled include:

Resin Component	Collection Media[*]	Sampling Rate, lpm	Total Volume, L	Analysis
Bisphenol A	GFF	1.0	180	NIOSH 333
Epichlorohydrin	CT, 100/50	0.01-0.2	2L @ 2ppm - 30L	NIOSH 1010
Methylene dianiline	GFF, treated	1.0	100	OSHA 57
Formaldehyde	CT, 100/50 coated	0.01-0.1	1L @ 3ppm - 36L	NIOSH 2541/5318
Styrene	CT, 100/50	0.1-1.0	5-14	NIOSH 1501

[*] GFF = glass fiber filter   CT = charcoal tube   L = liters   lpm = liters per minute

Always consult the manufacturer's MSDS for the resin system or prepreg to determine what sampling may be needed.

PERSONAL PROTECTIVE EQUIPMENT AND
ENGINEERING CONTROLS

The following information is provided as a guideline. Implementation of engineering controls or requirements to wear personal protective equipment (PPE) must be based on sound industrial hygiene evaluation of the process and valid air sampling data. Consulting applicable MSDS and manufacturer's product literature will also be helpful.

ENGINEERING CONTROLS

Tools used for machining composite materials should be equipped with local exhausts (preferably HEPA dust collection systems) to collect dusts at the point of generation. For portable hand tools (e.g., saws, drills, routers, grinders), high velocity-low volume (HVLV) exhausts are strongly recommended. HVLV systems also allow freedom of movement when working on large composite parts or intact aircraft. An acceptable alternative is the dust control system available from some manufacturers (e.g., Nilfisk) that integrates a vacuum unit with the hand tool. Permanently mounted dust producing equipment (e.g., band saws) should have exhausts that meet the installation and performance requirements in ACGIH (1988 or most current edition). In addition, machining should be done using wet methods whenever possible if local exhausts do not control dust generation.

Likewise, resin component mixing should be done in a laboratory hood or comparable ventilated enclosure (e.g., slotted backdraft hood). For layup operations, a downdraft table provides excellent ventilation when working on small parts. For larger component work, a booth similar to a paint spray booth may be the best alternative.

Further, air in composite facilities shall not be recirculated to other work areas. Local exhaust ventilation systems in machining areas should have in-line high efficiency particulate air (HEPA) filters with standard prefilters to prevent buildup of combustible dusts and residues.

If curing ovens or autoclaves operating above 350EC are used, purging with nitrogen gas has been found to decrease the occurrence of fires. Water drums for fire control should be placed in the curing area.

Where resin mixing occurs, there is a possibility for exothermic reactions to occur. Quenching facilities, as well as emergency standard operating procedures, should be available in this area. All personnel should be thoroughly trained in exotherm emergency protocol.

Proper use of engineering controls will not only prevent personnel exposures, but will alleviate the need for spark and explosion proof electric fixtures, fans, motors, etc.

All design plans for new composite facilities or changes to existing shops should be reviewed by the cognizant industrial hygienist (IH). Ventilation systems should be evaluated to ensure sufficient capture velocity before new shops open. Once work begins, the cognizant IH shall evaluate controls and work procedures in progress, and conduct personal sampling to assess airborne contaminants. Further recommendations may be warranted based on the survey results.

PERSONAL PROTECTIVE EQUIPMENT

The following recommendations are made for personnel working with advanced composite materials. As always, adjustments may be needed after the cognizant IH evaluates the materials, operation duration, operational procedures, engineering controls, etc. that are used in the repair shop. The recommendations are divided into those for fibers and those for the chemicals. Should a single person be doing the entire repair operation, the PPE can be consolidated to protect from both contaminants.

Fibers

Skin protection - Wear coveralls, preferably disposable (Tyvek® or equivalent, e.g., MIL-C-87069). If reusable coveralls are worn, they should be laundered separately from other clothing before wearing again. Coveralls should be vacuumed with a HEPA vacuum before removing or washing.

Leather gloves, though cumbersome, may be needed when handling raw cloth/yarn/tows for layups, or for working damaged areas on the aircraft where fibers may project outward. This is especially true for those fibers that have been shown to penetrate skin easily (e.g., boron).

Eye protection - When machining cured composites, safety glasses with side shields should be worn. Full face shields may be needed for large operations. An emergency eyewash station must be installed within 100 feet of machining operations.

Respiratory protection - Respiratory protection may be warranted based on air sampling data. If needed, the minimum recommended protection is a half mask with dust/fume/mist cartridges.

Resin components, solvents, prepreg composites

   Skin protection - To prevent skin defatting and skin absorption, wear impermeable gloves (butyl rubber, nitrile, or as recommended by the manufacturer based on the resin components). As a minimum, aprons should be worn to protect the body from splashes; coveralls are recommended.

   Eye protection - As a minimum, wear chemical splash goggles. Full face shields may be needed for some operations. An emergency eyewash/deluge shower must be installed within 100 feet of mixing and layup operations. It is recommended that the eyewash/shower be within 10 feet if the resin formulation has extremely reactive ingredients.

   Respiratory protection - Respiratory protection may be warranted based on air sampling data. If protection is required, the minimum respirator is a half mask with cartridge selection based on the specific solvent or resin components.

HYGIENE AND HOUSEKEEPING

   Personnel should always wash thoroughly with soap and water before breaks and at the end of the work shift. Do not allow eating, drinking or smoking in any composite work areas.

   Keep all work areas free of spills, dust and debris. Resins are usually viscous and may require special cleanup procedures.

   To remove dust and debris, the work area should be thoroughly vacuumed at the end of each work day. Use of a HEPA vacuum is strongly recommended. **NEVER** dry sweep or use forced air to clean composite dusts.

   Fully cured waste material, contaminated coveralls, vacuum filters, etc. should be disposed of as non-hazardous solid waste.   Place in drums or double bagged, sealed and disposed of in accordance with all Navy, local, state and Federal guidelines. Mark all disposal containers with a label that reads: "COMPOSITE WASTE. DO NOT INCINERATE. DO NOT SELL FOR SCRAP." For chemical wastes, consult applicable local, state, Federal and Navy guidance.

COMPOSITES IN FIRES

   The primary exposure concerns during a composite fire will change during the sequence of events that follow the mishap. If crash only is involved, protection is needed for fiber exposure. If there is a fire, vapors and aerosols generated by the burning resin may soon be followed by airborne fibers or particulates that have been freed from the

matrix. Should explosion occur, it is almost certain that respirable airborne fibers will be released.

   Some general mishap procedures will go a long way in protecting both personnel and the environment. The following guidance has been compiled from Margulies et. al. (1981), NAVAIR (1983), NAVENVIRHLTHCEN (1988), Naval Safety Center (1990) and Bischoff (1991).

! Only essential personnel should be allowed on the crash site.

! Whenever possible, all work should be done upwind of the crash site.

! As soon as the fire is extinguished and the wreckage has cooled, the debris should be sprayed with a fixative, such as polyacrylic acid (PAA). A light oil mist, acrylic floor wax or an equivalent tacky substance are acceptable substitutes.

! Do not allow eating, drinking or smoking in the crash vicinity.

! Personnel should shower as soon as possible after leaving the crash site.

! Exercise caution when handling debris. Skin punctures from reinforcing fiber splinters are possible.

! Hard surfaces (concrete, asphalt) in the impact area should be vacuumed or washed down. When washing, collect effluent in drainage trenches lined with burlap or mesh, then cover with dirt. For ship mishaps, wash all surfaces and drain overboard.

! Only firefighters should be allowed in the accident area while wreckage is still burning or smoldering.

! PPE recommendations:

   Firefighters - Requirements for firefighters are established in NAVAIR (1983) and Naval Safety Center (1990).

   Investigation and cleanup crew - wear Tyvek® or comparable coveralls, taped at the openings. Puncture resistant leather gloves are necessary when handling fibrous debris. Chemical resistant gloves are needed when there is a potential for contact with fuel or other fluids (e.g., hydraulic fluids). Personnel should wear steel toed boots. Non-vented goggles or safety glasses with side shields will provide eye protection if a full face respirator is not used.

   Personnel present during the early stages of investigation, when there may be unknown concentrations of airborne fibers and/or combustion byproducts, should wear

a full face respirator with high efficiency particulate air-organic vapor cartridges. After the debris is fixed and vapor/mist generation is no longer a concern, dust/fume/mist cartridges are appropriate unless sampling warrants greater protection.

All debris, vacuum bags, coveralls, etc. should be placed in drums or double bagged, sealed and disposed of in accordance with all Navy, local, state and Federal guidelines. Mark all disposal containers with a label that reads: "COMPOSITE WASTE. DO NOT INCINERATE. DO NOT SELL FOR SCRAP."

TOXICITY OF ADVANCED COMPOSITE MATERIALS

Advanced composite materials are in demand because they are stronger than steel yet more lightweight than aluminum. Their use, particularly in the aerospace industry, has skyrocketed over the past twenty years. Though initially aware of the potential health hazards from the resin components and solvents, manufacturers and end users dismissed the fibers as being much too large to be inhaled. It wasn't until the late 1970s that questions were raised about the dusts produced when cured composites were abraded. Consequently, the research on the toxicity of the composites is limited. Further, much of the information that is available has focused only on the carbon reinforced epoxy composite system.

Based on the limited composite fiber toxicological information available, aramid fibers seem to have the highest hazard potential. However, experiments yielding the positive data have used specially prepared fibers that may not be representative of those actually encountered in the workplace.

The evidence for silicon carbide, fibrous glass and carbon is so limited that categorizing the hazard potential is, at best, difficult. Data is available to support both sides of the argument, but is restricted in scope and reflective of short-term investigations.

When reviewing the toxicological data, keep in mind that most of the particulate produced during composite machining operations is not fibrous. In fact, several of the studies conclude that experimental animal tissue response is typical of a nuisance dust exposure. Particulate dimensions of the challenge material are given whenever available.

There have been no reports associating any of the composite reinforcing fibers with teratogenicity or reproductive hazards. There is one study that cites the mutagenic potential of pitch based carbon fibers (see in vitro section).

EPIDEMIOLOGICAL STUDIES

Fibers

Jones et. al. (1982) evaluated 88 employees at a PAN continuous filament carbon production plant. Thirty-one of the workers had been at the plant for over 5 years. Of the 8 abnormal chest X-rays seen, 4 were from employees who had worked at the plant longer than 5 years. However, none of the abnormalities was indicative of dust related disease. Spirometry testing showed no significant differences between observed and expected results for the forced expiratory volume/forced vital capacity ratio.

Air samples collected at the plant during 1979 and 1980 were considered representative and used as exposure data. The sampling methodology was such that only particulate #7Fm aerodynamic equivalent diameter (D_{ae}) was collected; samples were reportedly mostly non-fibrous material. Non-respirable fibers (diameter 8-10Fm) were noted to fracture laterally only. The highest mean total dust sample was 0.39 mg/m³; the highest mean respirable result was 0.16 mg/m³.

Though this study found no evidence of ill effects of carbon fibers or dusts on the lungs of employees, the authors note that the longest employee exposure period - 10 years - was still much too short when considering that a 20-30 year latency is needed for asbestos effects to surface.

The only other epidemiological evidence for reinforcing fibers results from the man-made vitreous fiber (MMVF) investigations, specifically those for fibrous glass. Though most insulating glass has a much smaller diameter than does reinforcing glass, some large diameter glasses were included in the studies. Such work is summarized here, with detailed information available in NAVENVIRHLTHCEN (1990).

A European epidemiological study has been following a total of 25,146 workers from 13 manufacturing plants located in seven countries. Two continuous filament production plants were included. Workers were entered in the study upon employment (ranging from 1950 to 1955). The initial report (Saracci et. al., 1984) followed the cohort through 1977. The followup in Simonato et. al. (1986) reported cohort analysis for 1981-1983 and included correctional factors not previously employed (i.e., standard mortality ratio adjustments for local and regional mortality rates). Simonato et. al. (1987) provided further update information. There was no evidence that continuous filament workers were subject to increased risks for development of lung cancer or other non-malignant disease.

Environmental surveys conducted from 1977-1980 by Ottery et. al. (1984) at the continuous filament plants found that the average respirable fiber exposures were <0.01 f/ml. Nominal fiber size was found to be 9-25Fm.

In the United States, 17 production plants have been studied, including 3 glass filament plants and 2 plants that produced both glass wool and filament. Workers had to be employed in production or maintenance for at least one year for entry in the cohort.

Preliminary reports (Enterline et. al., 1981; Enterline et. al., 1983; Enterline and Marsh, 1984) followed the cohort through 1977 and concluded that there was no correlation between glass filament production and respiratory cancers. The five year update (Enterline et. al., 1987) extended the study by looking at production by groups of fibers. There were no positive relationships for continuous filament workers and increased mortality or increased chance of developing lung cancer. Mean fiber exposures were reported as 0.11 f/cc.

The newest update (Marsh et. al., 1990) concludes that there is even weaker cumulative evidence for correlation between lung cancer mortality and MMVF exposures overall.

A respiratory health study by Weill et. al. (1983) assessed data gathered from 931 continuous filament fibrous glass workers via questionnaires and medical examinations (504 workers from plants producing glass fibers >3Fm diameter and 327 from plants producing 1-3Fm diameter filaments). No evidence was found of respiratory effects in the population, nor was there any discernible correlation between symptomology and fiber exposures.

Resins

Chemicals used in fibrous glass composite manufacturing were investigated after personnel reports of unusual symptoms. Though the study was a workman's compensation investigation and precluded the use of comparable control groups, the information is valuable within the given parameters.

Sparks et. al. (1990) report that employees began complaining of symptoms after a fibrous glass/phenol formaldehyde composite was introduced at the plant. Symptom onset ranged from one week to six months after the new material use was initiated. Symptoms included dizziness, nausea, headache, cognitive impairment, fatigue and palpitations. Work operations consisted of hand layup, oven curing and machining on cured composites.

Clinical evaluation of 53 employees involved occupational and medical history, physical and neurological examination, blood analyses and spirometry. Most workers were also evaluated by an allergist. Dermatological assessments were included for those with dermatitis.

Overall, reported symptoms did not vary significantly between job category, duration of exposure or location in the plant. Immunological assays for human serum albumin-formaldehyde complexed antibodies were unremarkable, as were other blood tests and physical exam results. Though neuropsychiatric evaluations showed a high degree of anxiety and depression, there was no apparent explanation for the exhibited symptomology.

Air sampling results were also unremarkable:

phenol - 0.001 - 0.180 ppm
formaldehyde - 0.003 -0.073 ppm
total particulate - 0.48 - 1.1 mg/m³
antimony trioxide - below detectable levels
styrene - below detectable levels - 1.2 ppm
acetone - below detectable levels - 7.6 ppm
methylene chloride - below detectable levels - 0.1 ppm

The investigation was unable to attribute symptoms to a specific cause. The report did note some parallel cases of "panic disorders" associated with exposures to chemicals that elicit respiratory irritation and that have a noxious odor. Many of the early complainants in the production plant had been referred to an allergist who sparked national media attention by announcing that some of the plant personnel had brain damage typical of that seen after exposure to toxic chemicals.

IN VITRO STUDIES

According to the studies conducted by Conning et. al. (1971), there is a direct relationship between dust induced cytotoxicity to macrophages and the occurrence of dust induced fibrogenicity in animals. To test this theory, Styles and Wilson (1973) incubated dust suspensions, including a carbon sample, with macrophage cell cultures for a total of two hours. The carbon concentration was 3.75×10^{-6} per milliliter; carbon particle diameter was 0.2-15Fm. Aliquots were examined at 0, 1 and 2 hours after the dust addition.

Less than 2% of the peritoneal macrophages died after phagocytizing the carbon particles, and less than 5% of the alveolar macrophages were dead at the end of the incubation time. Final test results (2 hour samples), including chrysotile and polyester controls, are shown below:

	Peritoneal Macrophages[*]			Alveolar Macrophages[*]		
	Carbon	Chrys.	Poly.	Carbon	Chrys.	Poly.
% live cells	94.4 ± 0.8	88.8 ± 2.7	95.2 ± 2.1	86.4 ± 2.2	78.1 ± 3.2	88.4 ± 2.0
% cells with particulate	49.9 ± 5.0	49.5 ± 12.1	41.0 ± 6.5	34.0 ± 4.3	21.7 ± 3.1	31.3 ± 3.3
% dead cells with particulate	7.9 ± 0.9	47.6 ± 5.5	5.1 ± 1.7	8.7 ± 3.6	60.3 ± 0.7	6.1 ± 1.8
% dead cells with particulate (as % of all cells with particulate)	0.9	10.8	0.6	3.5	60.9	2.3

[*] Chrys. = chrysotile   Poly. = polyester

These results support the idea that fibrogenicity of a dust is related to its toxic effect in vitro. Chrysotile, a known fibrogenic fiber, caused the highest macrophage cell death rate, whereas the non-fibrogenic polyester induced low cell death rates. The carbon dust sample results parallel those of the polyester.

Richards and Hunt (1983) incubated rabbit lung fibroblasts with various concentrations of ground carbon fiber cloth (90% of the fibers <10Fm long) in saline suspension. After 24 days, they assessed deoxyribonucleic acid (DNA) and cell mat hydroxyproline levels as indicators of cell deterioration. Based on the results, the authors concluded that carbon was expected to be inactive in the in vivo induction of fibrogenicity.

Richards and Hunt (1983) concluded the report with the statement that their in vitro methodology might not be adequate to correlate with in vivo fibrogenicity. The reason for the caveat was that their results conflicted with other published reports on reactions of known fibrogenic dusts. The Richards and Hunt data follows:

	Results[*] (Reactive Dose Given)	
Sample Material	DNA	Hydroxyproline
Normal results	8 to day 10; steady to day 20; 9 after 25	steady 8 to day 25
UICC chrysotile	8 (100Fg)	9 (250 Fg)
Carbon	NSE	NSE
Quartz	8 (500Fg) (8 directly related to dose)	9 (500Fg)
Activated Charcoal	NSE	NSE
Titanium dioxide	NSE	9 (500Fg)

[*] NSE = no significant effect   8 = increase   9 = decrease

Using the same composite dusts that were characterized by Boatman et. al. (1988) (see page 34 of this report), Martin et. al. (1989) evaluated in vitro cytotoxicity. Respirable fractions of the dusts, final concentration 500Fg/ml, were incubated with rabbit lung macrophages. Toxicity was evaluated using (1) trypan blue exclusion - assessment of cell viability and integrity, (2) ^{51}Cr release - measurement of loss rate of labelled intracellular proteins, and (3) particle ingestion counts - accounts for any result differences based on the macrophage's ability to phagocytize the particle. The dusts were . 74% <3Fm aerodynamic equivalent diameter (D_{ae}) and 99.9% <10Fm D_{ae}. From the data (summarized in the following table), the authors concluded that PAN graphite/-epoxy/aromatic amine and pitch graphite/epoxy/aromatic amine were the most cytotoxic, though not as toxic as quartz. The PAN graphite/epoxy/amine was equivalent to the negative control; graphite/PEEK and PAN graphite-Kevlar®/epoxy/amine were intermediate in their toxicity. Cyto-toxicological differences were not attributable to the macrophage's ability to phagocitize the dusts.

Material, Cure Agent[*]	Avg.[*] D, Fm	Trypan Blue Exclusion[*]			^{51}Cr Release[*], %		
		2 hr	24 hr	48 hr	2 hr	24 hr	48 hr
graphite/PEEK	1.6	92.1	89.3	86.4	25.7	43.8	56.1
PAN graphite-Kevlar®/ epoxy, A	1.9	92.3	90.5	85.7	24.3	43.5	56.9
PAN graphite/ epoxy, AA	1.8	94.0	85.9	81.8	27.1	45.1	56.9
Pitch graph-ite/epoxy, AA	1.6	94.8	88.6	78.4	31.9	50.3	64.4
PAN graphite/ epoxy, A	1.1	94.4	94.2	92.1	30.4	36.8	48.6
Pure culture medium	--	93.1	95.3	96.0	23.6	33.7	42.9
Aluminum oxide (neg.)	--	93.7	94.5	93.3	21.4	35.4	47.2
Quartz (pos.)	--	92.0	66.4	58.0	29.1	63.7	72.6

[*] A = amine curing agent   AA = aromatic amine curing agent
D = diameter   Avg. = average   Hr = hours   neg. = negative control
pos. = positive control

Union Carbide conducted studies on the mutagenic potential of benzene extracts of pitch and PAN based carbon fibers (Hengler and Slesinski, 1982a, 1982b; Slesinski et. al., 1982, 1983). Fibers obtained by grinding were added to benzene in a 10% weight/volume (w/v) suspension. The benzene was removed after 14 days and the evaporate reconstituted in acetone. Extracts were evaluated using: (1) Ames bacterial assays, (2) Chinese hamster ovary (CHO) test to detect gene mutations, (3) sister chromatid exchange (SCE) to determine the interchange of genetic material between chromatids of individual chromosomes, and (4) determination of unscheduled deoxyribo-nucleic acid (DNA) synthesis in primary rat liver cell cultures, an indication of the capability of causing chromosomal damage. Doses varied for each test condition (overall range 0.003% volume/volume (v/v) - 3% v/v). All tests except DNA were done both with and without S9 metabolic activation.

PAN based carbon fibers were negative for all test conditions. Pitch based fibers were negative in the CHO and Ames assays. However, SCE for the pitch derived fibers showed a weak but statistically significant dose related increase in SCE over the range of test concentrations used. This occurred in both unactivated and activated tests. There was also a noticeable increase in the number of chromosomal aberrations.

In addition, the pitch fibers showed significant levels of radioactive thymidine incorporation over the 167-fold range of test concentrations. These results led to the conclusion that pitch based carbon fibers were potentially mutagenic.

The authors caution that the fiber preparation conditions were atypical, and the chance for similar human exposure in the workplace is extremely remote.

In vitro tests with aramid fibers were performed by Dunnigan et. al. (1984), who extracted short fibers from Kevlar® 979, dry pulp and merge 6F218. Test fibers at concentrations of 0, 25, 50, 100 and 200Fg/ml were incubated for 18 hours with rat alveolar macrophages. Following incubation, the suspensions were tested for lactic dehydrogenase (lysosomal enzyme release), beta galactosidase (cytoplasmic enzyme release) and adenosine triphosphate (index of cell viability). The average size of the test fibers was 0.138Fm diameter x 2.72Fm long; 90% of the fibers were #0.25Fm diameter x 5Fm long.

The test aramid fibers elicited essentially the same response as chrysotile when fresh macrophages were used. When 24 hour cell cultures were inoculated, cytotoxic response was greater for aramid fibers than that of chrysotile.

A continuous filament fibrous glass composite sample was included in the in vitro studies of Martin et. al. (1989). The respirable sample was obtained from a spindle shaping operation on a fibrous glass/epoxy/amine curing agent composite. The average fiber length was 262Fm (32-2500Fm range), with an average 10Fm diameter and a 26:1 aspect ratio. Trypan blue exclusion experiments were not completed due to insufficient amounts of respirable material.

After 48 hours incubation with rabbit alveolar macrophages, [51]chromium release results were: 2 hours - 25.1%, 24 hours - 40.2% and at 48 hours - 54.8%. These results parallel those of the aluminum oxide negative control (2 hours - 21.4%; 24 hours - 35.4%; 48 hours - 47.2%).

Because of the research associated with the man-made vitreous fibers, there is more extensive information available on fibrous glass than on the other reinforcing fibers. Tilkes and Beck (1980; 1983) looked at cytotoxicity in relation to fiber dimensions. They measured LDH and beta glucuronidase to monitor changes in plasma and lysosomal membrane permeability. The study used both rat and guinea pig lung macrophages exposed to fibrous glass. The authors concluded that cytotoxicity was dependent on the

fiber's length and diameter. Whereas short fibers were only toxic when they were <0.03Fm in diameter, long and thin glass fibers were as toxic as chrysotile and crocidolite.

   Using hamster embryo cells, Hesterberg and Barrett (1984) also found that cell transformations were dependent on fiber dimensions. When glass fiber lengths were held constant and diameters varied, the thinner fibers (average 0.13Fm) were 20 times more toxic than fibers with diameters in the 0.8Fm range. When diameters were kept constant and length varied, cell transformations decreased ten fold as the length decreased from 9.5 to 1.7Fm. No cytotoxicological changes were noted when fiber were less than about 1Fm long.

   The ability of long, thin glass fibers to induce cell transformations has been documented by others (e.g., Brown et. al., 1979a, 1979b; Chamberlain et. al., 1979; Pickrell et. al., 1983). However, remember that fibrous glass reinforcing fibers have average diameters greater than 9Fm.

   Chamberlain and Tarmy (1977) found that glass fibers do not appear to induce gene mutations in bacterial cell lines. Sincock et. al. (1982) reported that fibrous glass did cause chromosomal aberrations and transformations in cultured fibroblasts, but the effects were much less severe than those cause by asbestos.

   In vitro studies by Lipkin (1980) showed that silicon carbide (SiC) fibers were highly cytotoxic. He used the P388D1 cell line, previously shown to exhibit dose dependent cytotoxic effects with asbestos fibers (e.g., Wade et. al., 1976, 1978). Using these macrophage-like cells to test various other fibers, including borosilicate, aluminum oxide and dawsonite (dihydroxysodium aluminum carbonate), Lipkin concluded that silicon carbide had a high probability (1.0) of inducing sarcomas in vivo. Katz (1980) supports these findings.

   Birchall et. al. (1988) also agrees. He prepared SiC whisker samples containing both fibrous (97% of fibers 0.05Fm diameter) and nonfibrous components. The samples were extracted and washed to eliminate any free silica, then incubated with Chinese hamster lung cells. The SiC dose response curve paralleled that of the crocidolite control. Additional tests on SiC powder (average particle size 0.4Fm) were all negative, indicating that the fibrous portion of the samples was responsible for the toxicity.

ANIMAL STUDIES

   Animal studies must be viewed with some caution. Though results obtained by artificial introduction of the material are valuable in assessing overall hazard potential, it is important to remember that it is the inhalation of the composite fibers and dusts that are

of concern. Consequently, the animal data is separated by method of fiber introduction -implantation, injection and inhalation.

Implantation

   Implantation and equivalent research on carbon is largely based on attempts to evaluate carbon's potential as a prosthetic device material. Bowman et. al. (1977) implanted carbon fibers in 100 rats and 100 mice, evaluating the results after 24 months and 18 months, respectively. Fiber sizes were not given, but the report stated that the fibers were commercially available. One malignant tumor, a fibrosarcoma, developed as a result of the implant.

   Tayton et. al. (1982) implanted carbon filaments (1.5 cm long) intramuscularly in 50 rats. In addition, 5 cm lengths were tied around the mid shaft periosteum of the left femur of 10 rats. Animals were sacrificed at 18 months and examined for reaction. In all cases, fewer changes were observed in the carbon test animals than in the silk suture negative control animals. Tissue reactions were unremarkable, showing no inflammation and no evidence of malignancy. Implant areas were surrounded by fibrous tissue, and carbon debris was noted in interstitial spaces and in macrophages.

   Stanton et. al. (1977; 1981) implanted rats intrathoracically with 40 mg doses of 12 different fibers, including specially prepared SiC whiskers (#8Fm diameter x .01 - >64Fm long) and varying sizes of fibrous glass (.01 - >8Fm diameter x .01 - >64Fm long). The animals were followed for two years. Pleural tumors in the glass test group varied from 0 in 115 animals to 20 in 29 animals. Silicon carbide treated animals had a 17/26 tumor incidence. Also reported was the finding that the most carcinogenic fibers were less than 0. 25Fm in diameter and greater than 8Fm long, although there were also high correlations for fibers that were less than 1.5F diameter x >8Fm long.

Injection

   Luchtel et. al. (1988; 1989) report the animal studies that correlate with the machining dust characterizations by Boatman et. al. (1988) and the in vitro work by Martin et. al. (1989). Male rats received single intratracheal injections of 5 mg respirable machining dust samples suspended in 0.25 milliliters (ml) phosphate buffered saline. All animals were sacrificed at 1 month and histopathological examinations done on the left lung. Slides were reviewed "blind" and graded from 0 (negative) to 4 (marked pathology, extensive infiltration, striking accumulation of alveolar macrophages, extensive fibrosis and nodules). Results are summarized below.

Test Material (Curing Agent)	Results/Comments	Score (Range)
Graphite/PEEK	low histological response, similar to aluminum oxide	1.2 (1-1.5)
Graphite (PAN)-Kevlar®/ epoxy(amine)	low histological response, similar to aluminum oxide	1.2 (1-1.5)
Graphite (PAN)/epoxy (aromatic amine)	small fibrotic nodules	2.7 (2.2-3)
Graphite (pitch)/epoxy (aromatic amine)	small fibrotic nodules	1.6 (0-2)
Graphite (PAN)/epoxy (amine)	small fibrotic nodules	1.4 (1-2)
Sodium chloride (negative control)	negative	0 (0-0)
Quartz (positive control)	accumulation of protein material, fibrotic lesions, macrophages in lung	3.7 (3.2-4)
Aluminum oxide (inert material control)	increased number of macrophages, no lesions	1.1 (1-1.5)

These results, coupled with those of Martin et. al. (1989), led to the following toxicity rankings for the tested composite materials:

Rank	Test Material	Overall Score
1	Sodium chloride	5
2	Aluminum oxide	10
3	Graphite (PAN)-Kevlar®/epoxy (amine)	15
4[*]	Graphite (PAN)/epoxy (amine)	18
5[*]	Graphite/PEEK	27
6[*]	Graphite (PAN)/epoxy (aromatic amine)	35
7[*]	Graphite (pitch)/epoxy (aromatic amine)	38
8	Quartz	45

[*] The authors note that numbers 4 and 5 could be reversed and numbers 6 and 7 could be reversed.

The reasons for toxicity differences were not clear, but the cumulative study results suggest that the toxicity could be based on, or at least greatly influenced by, the resin material and/or the curing agent. Notice that the highest ranked samples had similar resins and aromatic amine curing agents, whereas the lower ranked dusts had different curing agents and one also had a different resin material.

Styles and Wilson (1973) injected 12 rats intraperitoneally with 50 mg/kg body weight of carbon dust suspensions (10 mg dust/ml saline). The animals were killed after three months. No lesions were observed for carbon injected animals. Polyester negative control animals exhibited granulomatous lesions and chrysotile controls developed fibrotic nodules.

Carbon fiber reinforced carbon prosthetic device fragments, 7Fm diameter x 20-100Fm long, were suspended in saline and injected in the medullary space of rabbit femurs (Neugebauer et. al, 1981). Pathological examination of animals sacrificed at 2 weeks showed that smaller particles had been phagocytized, with the remaining fragments randomly deposited. There was some fibrosis in the deposition area, but no evidence of destruction of the neighboring bone.

Twelve weeks after the injection, microscopic evaluation revealed continued minimal fibrosis, foreign body giant cells and newly formed bone in the immediate vicinity of the injection. There was no tissue necrosis, although carbon particles were found in the lung, liver, spleen and kidneys of the test animals.

Tayton et. al. (1982) used carbon filaments ground to a powder and suspended in saline for intamuscular injection in rats. Each was injected with the powder equivalent of a 1.5 cm length of carbon fiber. After 18 months, examination revealed carbon fragments in the muscle interstitium. There was evidence of minor fibrosis, but findings were otherwise unremarkable.

An aramid fiber was included in the evaluation by Pott et. al. (1987) of intraperitoneal and intratracheal injections in rats of 50 different dusts. The Dupont Kevlar® intraperitoneal sample was specially prepared with ultrasonic treatment in an attempt to obtain individual fibers. Injections were given once a week - 2 mg in week one, and 4 mg each for week two and three. Animals were held until natural death. Results were:

Test Material	Number of Rats	Results[*], % Animals with Tumors
Sodium chloride	32	6.3
UICC chrysotile	32	84.4
Kevlar®	31	12.9

[*] Only sarcomas, mesotheliomas or carcinomas of the abdominal cavity were reported.

Intratracheal injection fibers were dried and milled before ultrasonic treatment. Dimensions of the fibers were 50% <3.9Fm long, 50% <0.47Fm in diameter. Injections were given weekly for 5 weeks at 4 mg per week. Tumor incidence at 28 months post injection was:

Test Material	Number of Rats	Results[*], % Animals with Tumors
Sodium chloride	102	2.0
UICC chrysotile	34 36 36	61.8 19.4 86.1
Kevlar®	52	5.8

[*] Only sarcomas, mesotheliomas or carcinomas of the abdominal cavity were reported.

The report cautions that a homogeneous suspension of Kevlar® was not obtained in either experiment. The injected fibers were in clumps rather than single fibers.

Vu (1988) cites a study in which three groups of rats received single intraperitoneal injections of commercial grade Kevlar® pulp in saline at 0.25, 2.5 and 25 mg doses (Davis, 1987). As in the Pott et. al. (1987) studies, the bulk of the injection material was in clumps. After 9 months, there were 2 peritoneal mesotheliomas in the 25 mg group (total 32 rats), 0/32 at 2.5 mg and 0/48 at the 0.25 mg dose. Untreated control animal results were 0/48. Note was made of some cellular granulomas of macrophages, fibroblasts and foreign body cells.

Pott et. al. (1989) again used Kevlar® in an intraperitoneal injection study of fibrous and granular dusts. The Kevlar® was sized as 90% <12Fm long and 90% <0.76Fm diameter. Sizing was done only on fibers with an aspect ratio greater than 5:1. Rats were injected weekly for 5 weeks with a suspension of 4 mg dust in saline. Animals were sacrificed at 130 weeks.

The authors again noted the difficulty in obtaining single fibers. Tumor incidence (tumor defined as mesothelioma or sarcoma of the abdominal cavity) was:

Test Material	# Tumors/# Rats	% Tumor Occurrence
Kevlar®	3/53	6
Chrysotile	12/36 23/34 30/36	33 68 83
Sodium chloride	2/102	2
Polypropylene	2/51	4

Dupont Nomex® was evaluated by Reinhardt (1980) in an intratracheal instillation study. The sample, 2.5 mg of shredded and ground Nomex® (2-30Fm diameter x 2-100Fm long) was suspended in saline and a single dose given to the test rats. Respiratory tract histopathological examinations were done at 2 days, 7 days, 3 months, 6 months, 1 year and 2 years post instillation. Though the Nomex® did not produce any tumors, foreign body granulomas and nonspecific dust reactions were attributed to the large non-respirable particles. All tissue reactions decreased in severity with increasing post treatment time, with animal lungs appearing normal at the 2 year examination.

Luchtel et. al. (1988; 1989) included a fibrous glass/epoxy (amine curing agent) dust in their intratracheal injection studies. After 1 month, animals exposed to the fibrous glass dust had developed small fibrotic nodules. The average score for all slides reviewed was 2.5, with a range of 2-2.8 (0 = negative; 4 = marked pathology). Average score for the sodium chloride negative control was 0 and for the quartz positive control was 3.7. The authors noted that the fibrous glass sample caused more severe and diverse pathological changes overall than did any of the graphite samples included in the study (see page 75 for graphite results).

Two groups of "large" glass fibers (1.5Fm diameter x 5Fm long and 1.5Fm diameter x 60Fm long) were instilled intratracheally in the Drew et. al. (1987) study. Animals received 10 weekly doses. Macrophage aggregation and granulomatous foreign body response was noted, but there were no tumors nor was there any effect on rat mortality.

The Pott et. al. (1987) study included varying doses (10-250 mg) of three size groups of glass fibers: (1) 80% 3.3-4.2Fm diameter, median length 16.5Fm; (2) 80% 4.8-6.3Fm diameter, median length 39Fm; and (3) 89% 6.8-8.1Fm diameter, median length 46Fm. There were no statistically significant increases in the incidence of sarcomas or mesotheliomas in test animals when compared with the negative controls.

Single intrapleural injections of glass fibers (maximum diameter 7Fm, 60% >20Fm long) in rats produced no tumors (Wagner et. al., 1973).

Though not truly injection experiments, the Union Carbide (1981; 1982; 1983) and Depass (1982) skin painting studies are most appropriately discussed in this section. PAN and pitch derived carbon fibers were pulverized and suspended in benzene (10% w/v). The suspensions were applied three times per week (25Fl per application) to the shaved backs of mice. The experiments included four test fibers and a positive and negative control. Each sample was tested on 40 mice, ranging from 51-76 days of age at the first application. The painting continued until the natural death of the animal.

Only the papilloma and squamous cell carcinomas from the pitch based carbon were considered related to the application site. The authors suggest that these tumors were produced as a response to a tumor promoting activity - that is, epidermal hyperplasia secondary to a local irritation - rather than as a direct chemical carcinogenic response. The report also notes the absence of an untreated control group to assess the number and types of spontaneous tumors and the natural mortality rates. The experimental results are summarized in the following table:

Test Material	Results Summary
3-methylcholanthrene, 0.1% suspension in acetone (positive)	Mean survival 204 days. Early mortality due to high incidence of death from skin tumors. First tumor 31 days post treatment. 2 papillomas, 33 squamous cell carcinomas of the skin.
Undiluted benzene (negative)	Mean survival 435 days. No tumors.
Pitch carbon, continuous filament (Thornel® type P), 1.9 mg/application	1 skin papilloma at 236 days. 1 skin squamous cell carcinoma at 294 days. 1 subcutaneous hemangiosarcoma.
MAT pitch carbon (Thornel® mat, short fibers), 2.0 mg/application.	0 tumors at application site. 3 tumors at remote sites, first seen at 579 days (1 subcutaneous squamous cell - inguinal; 1 skin fibrosarcoma - axilla; 1 hemangio-sarcoma, subcutaneous, abdominal)
PAN carbon continuous filament, 1.1 mg/application	0 tumors
PAN oxidized carbon continuous filament, 1.3 mg/application	0 tumors at application site. 1 leiomyosarcoma of shoulder at 613 days.

Inhalation

    Composite fiber inhalation studies are best presented in summary tables. Much of the data represents short term studies - a few weeks or months - that report only macrophage and inflammatory responses. Very few of the analyses are animal lifetime evaluations that report tumor occurrence. The exception is the data on fibrous glass, again more extensive because of the man-made vitreous fiber investigations.

    The following legend applies to the tables:

Exposure schedule: h = hours   d = day   w = week   m = month   y = year

Fiber size: d = diameter   l = length

Response: BA = bronchioalveolar adenoma   E = epidermoid carcinoma
          SCC = squamous cell carcinoma   M = mesothelioma
          B = bronchial carcinoma

Reference Exposure Dose and Schedule	Test Animal	Fiber Type	Fiber Size	Results/Comments
Holt and Horn (1978)	Guinea pig	PAN carbon	98.8% non-fibrous respirable carbon.	Animals sacrificed periodically up to 144 d
Respirable dose: 370 particles/ml of air for non-fibrous particles; 2.9 particles/ml for "black" fibers (carbon)			Fibers were 1-2.5Fm d, 15Fm l	
Exposure varied: 7h, 23h, 62h, 100h, 104h				No fibrosis seen. All fibrous particles >5Fmseen extracellularly except for 1 fiber >10Fm seen intracellularly.
Holt and Horn (1982) (extension of 1978 study)	Guinea pig	PAN carbon	Same as 1978 study	Intracellular dust seen up to 1 year post exposure
Exposure varied: 7h, 10h, 12h, 100h				No fibrosis, no lesions, no pathological effects.
				Carbon fiber bodies (ferroprotein coated C) observed.
Thomson (1987)	Rat	Synthetic graphite	Not given	Examined at 24h, 14d, 3m
1, 10, 100, 500 mg/m³				No significant histopathological changes. Fits nuisance dust category.
Exposure: 4h				
Plevan (1984); Owen et. al. (1986)	Rat	PAN carbon	7Fm d, 20-60Fm l (prepared by pulverizing in mill)	Examined at 4, 8, 12, 16, 32 w post exposure.
Dose: 20 mg/m³				No pulmonary fibrosis or inflammation. Only treatment related finding was black stained tails at 4-16w. Found carbon fibers in tail stratum corneum.
Exposure: 6h/d, 5d/w for 16w				

Reference Exposure Dose and Schedule	Test Animal	Fiber Type	Fiber Size	Results/Comments
Kanakia et. al. (1980)	Rat	Graphite/epoxy	Not applicable	Designed to assess smoke toxicity.
				Animals observed for 14 days post exposure.
Composite samples burned at 5 and 10 W/cm² heat flux. Five smoke concentrations tested for each flux.				5W/cm² 10W/cm² smoke conc. deaths smoke conc. deaths
Exposure: 30 minutes at each concentration				23.4 mg/L 0 28.0 mg/L 0 33.9 mg/L 1/6 36.8 mg/L 0 40.3 mg/L 6/6 37.8 mg/L 3/6 55.6 mg/L 6/6 38.3 mg/L 6/6 67.6 mg/L 6/6 43.4 mg/L 6/6
Kanakia et. al. (1980)	Rat	Graphite/BMI	Not applicable	5W/cm² 10W/cm² smoke conc. deaths smoke conc. deaths
Same exposures as above.				23.6 mg/L 0 21.0 mg/L 0 31.8 mg/L 3/6 24.0 mg/L 1/6 48.6 mg/L 6/16 32.5 mg/L 2/6 57.9 mg/L 0 40.3 mg/L 3/6 46.5 mg/L 5/6
Reinhardt (1980)				
150 mg/m³ for 4 h	Rat	Kevlar®	Not given - listed as "dust"	No deaths
130 mg/m³ 4 h/d, 5d/w for 2w	Rat	Kevlar®	Not given	Examined immediately after exposure and 14 days post exposure
				No deaths. Numerous macrophages seen at first examination; number decreased by 14 days. Typical nonspecific foreign body response.

Reference Exposure Dose and Schedule	Test Animal	Fiber Type	Fiber Size	Results/Comments
Lee <u>et. al.</u> (1983)	Rat	Kevlar® ultrafine	60-70% <1Fm x 10-30Fm	0.1 mg/m³ - rare alveolar macrophage (AM). Lung normal @ 2w. AM gone @ 6m.
0.1, 0.5, 3.0, 18 mg/m³			49-94% respirable	0.5 mg/m³ - aggregates of AM in bronchioles, alveolar ducts and alveoli @ 2w. Most AM gone @ 3m.
6 h/d for 5 d, 2d rest, 6h/d for 5 d				3.0 mg/m³ - high AM accumulation in ducts and bronchioles @ 2w; also minor inflammation & duct thickening. At 3m, dense AM in ducts. By 6m, patchy duct thickening.
0.1, 0.5, 3.0 mg/m³ animals sacrificed at 2w, 3m, 6m; 18 mg/m³ animals sacrificed at 4d, 2w, 1m, 3m, 6m.				18 mg/m³ - at 2w, dense AM & acute inflammation. Fibrotic thickening declining @ 3m. Almost normal appearance @ 6m.
Lee <u>et. al.</u> (1983)	Rat	Commercial Kevlar®	13% respirable mass (<5Fm D_{ae})	Results similar to the 3 mg/m³ exposures for ultrafine Kevlar®. Dense AM & inflammation @ 2w, followed by some duct wall tickening. At 6m, lungs appeared almost normal. Not considered fibrogenic.
18 mg/m³ (. 2.5 mg/m³ respirable)				
6 h/d for 5 d, 2d rest, 6 h/d for 5d				
Reinhardt (1985a; 1985b); Reinhardt (-1986); Lee <u>et.al.</u> (1988)	Rat	Kevlar®	>70% respirable. 90% <1.5Fm d; 95% <10Fm d; >70% <20F, l	Evaluations at 3m, 6m, 12m. All sacrificed at 2 years.
	NOTES:			Exposure, f/cc BA SCC
2.5, 25, 100, 400 f/cc (. 0.08, 0.31, 0.63, 2.23 mg/m³, respectively) Exposure: 6h/d, 5d/w, for 2y except 400 f/cc at 6h/d, 5d/w for 1y.	2.5 f/cc - most Kevlar® phagocitized by AM adjacent to alveolar duct region. 25 f/cc - Most fibrils seen in bronchioles & alveolar ducts. Some collagen fibrous granulomas in ducts. 100 f/cc - Fibrils densely deposited in bifurcations, bronchioles, ducts & alveoli. Patchy duct thickening. 400 f/cc - Granulomatous lesions in ducts @ 12m; most repaired by 2y.			0 1/137 0/137 2.5 1/133 0/133 25 1/132 0/132 100 4/137 4/137 400 4/92 7/92

Reference Exposure Dose and Schedule	Test Animal	Fiber Type	Fiber Size	Results/Comments
Mitchell et. al. (1986)				
15 mg/m³; 7h/d, 5d/w for 21 m	Rat	Fibrous glass,	4-6Fm d, >20Fm l	No tumors, no fibrosis
"		coated	0.5-3.5Fm d, >10Fm l	"
5 mg/m³; 7 h/d, 5d/w for 21 m	Rat	Fibrous glass,	<3.5Fm d, >10Fm l	"
"		uncoated	<3.5Fm d, <10Fm l	"
15 mg/m³; 7h/d, 5d/w for 18 m	Monkey	Fibrous glass,	4-6Fm d, >20Fm l	No tumors, no fibrosis
"		coated	0.5-3.5Fm d, >10Fm l	"
5 mg/m³; 7h/d, 5d/w for 18 m	Monkey	Fibrous glass,	<3.5Fm d, >10Fm l	"
"		uncoated	<3.5Fm d, <10Fm l	"
Lee et. al. (1981b)				
700 f/cc (ball milled)	Rat	Fibrous glass	0.2-6.5Fm d, <2Fm l	2/11 BA
Exposure: 6h/d, 5d/w for 90 d		Negative control		0/13
		Amosite	0.4Fm d, 5Fm l	2/11 BA, 1/11 E
	Guinea pig	Fibrous glas	0.2-6.5Fm d, <2Fm l	2/7 BA
		Negative control		0/5
		Amosite	0.4Fm d, 5Fm l	0/5
	Hamster	Fibrous glass	0.2-6.5Fm d, <2Fm l	0/9
		Negative control		0/7
		Amosite	0.4Fm d, 5Fm l	0/5

Reference Exposure Dose and Schedule	Test Animal	Fiber Type	Fiber Size	Results/Comments
Smith et. al. (1987)				
12 mg/m³; 6 h/d, 5d/w for 2 y	Hamster	Fibrous glass	5.4Fm median d	No tumors, no fibrosis
1.32 mg/m³; "		"	5.4Fm median d	"
9 mg/m³ "		"	6.1Fm median d	"
7 mg/m³ "		Crocidolite		No tumors, severe fibrosis
		Negative control		No tumors, no fibrosis
12 mg/m³; 6 h/d, 5d/w for 2 y	Rat	Fibrous glass	5.4Fm median d	No tumors, no fibrosis
1.32 mg/m³ "		"	5.4Fm median d	"
9 mg/m³ "		"	6.1Fm median d	"
7 mg/m³ "		Crocidolite		2/57 B, 1/57 M. Severe fibrosis.
		Negative control		No tumors, no fibrosis
Gross et. al. (1970)				
135 mg/m³	Rat and hamster	Fibrous glass/ phenol formalde- hyde resin	0.5Fm average d, >10Fm l	No tumors
Exposure: 6 h/d, 5d/w for 2y		Fibrous glass with binder	"	"
		Fibrous glass, uncoated	"	"
		Negative control	"	"

RESIN SYSTEM STUDIES

Toxicological data specific to composite resins is virtually nonexistent. There is information on individual resin chemicals, hardeners and solvents that can be reviewed elsewhere. SACMA (1991) includes a concise review of composite chemical toxicology. Other reference examples are IARC monograph publications, National Toxicology Program (NTP) reports, Registry of Toxic Effects of Chemical Substances (RTECS) and Sax (1984; 1987).

Peristianis et. al. (1988) evaluated the cutaneous and systematic carcinogenic potential of three commercially available epoxy resins: (1) pure diglycidyl ether of bisphenol A (2,2-bis[4-(2,3-epoxypropoxy)-phenyl]propane or DGEBPA; (2) Epon® 828 - DGEBPA[1], #29% epichlorohydrin; (3) Epikote® 828 - technical DGEBPA[2], #3 ppm epichlorohydrin.

Resin solution was applied to the dorsal skin of mice twice per week for two years at 0.2ml per application. The study included both 1% and 10% solutions of the epoxy resins in acetone. Each exposure scenario was conducted on 50 male and 50 female mice, except the negative control, which was done on 100 mice of each sex. Acetone was used as the negative control and 2% $-propiolactone in acetone served as the positive control. Results were based on full necropsy of all test animals.

The report noted a slight increase in renal tumors in male test mice that were treated with 10% Epon® 828, and an increase in the number of lymphoreticular/haematopoietic neoplasms (females only) with both pure DGEBPA and Epikote® 828.

Exposure to the epoxies had no effect on animal survivability when compared with control animals. Using the results shown on the following page, the author concluded that both Epikote® 828 and pure DGEBPA had a low order carcinogenic potential.

| | Number of animals with tumors | | | | | | | |
| | DGEBPA[1] | | DGEBPA[2] | | DGEBPA | | Neg | Pos |
Tumor produced*	1%	10%	1%	10%	1%	10%		
Squamous cell CA - M		1						113
Squamous cell P - B			1					24
Basal cell CA - M			1	2				16
Sebaceous gland A - B				1				2
Haemangiosarcoma - M						2		
Haemangioendothelioma-B			1					
Fibroma - B			1					
Fibrosarcoma - M		1				1	1	13
Anaplastic sarcoma - M					1			3
Sloughed tumors - B								13
Anaplastic CA - M								8
Trichoepithelioma - B								1
Keratoacanthoma - B								1
Lymphangioma - B								1
UNTREATED SITE TUMORS								
Basal cell CA - M				2	1			
Fibrosarcoma - M					1			
Squamous cell CA - M					1			1

* CA = carcinoma   P = papilloma   A = adenoma   M = malignant   B = benign

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